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TABLE OF CONTENTS (continued)

	Page	Russ. page
20. Stabilization of α-Halo Ethers. M. F. Shostakovsky and A. V. Bogdanova	133	162
21. Reactions Between Vinyl Compounds and Multifunctional Compounds. Communication 1. Reactions of Alkyl Vinyl Ethers with Glycerol. M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya	137	166
Brief Communications		
22. Synthesis of 1-Methyl-3-propylcyclobutane. B. A. Kazansky and M. Yu. Lukina	143	173
23. Synthesis and Reactions of Unsaturated Organosilicon Compounds. Communication 1. Synthesis of Vinylchlorosilanes by the Direct Method. M. F. Shostakovsky and D. A. Kochkin	145	174
Discussion		
24. Experimental Determination of Electron Density in Crystals. N. V. Ageev	147	176
Current Events		
25. Election of Academicians and Corresponding Members at The Academy of Sciences of the USSR	155	184
26. A. E. Chichibabin's "Fundamental Principles of Organic Chemistry", Volume I. I. L. Knunyants	165	204

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March-April, 1954

TABLE OF CONTENTS

	Page	Russ. page
General and Inorganic Chemistry		
1. Low-Temperature Modifications of Ammonium Nitrate, and Its Cooling and Quenching. S. I. Volfkovich, S. M. Rubinchik, and V. M. Kozhin.	167	209
2. Sorption of Water Vapor by Active Charcoals. M. M. Dubinin and E. D. Zaverina	175	217
3. New Method for the Investigation of the Mechanism of Cathode Processes, and Its Application. M. Smyalovsky and Z. Shklyarskaya-Smyalovskaya.	179	225
4. Investigation of Cathodic Polarization Occurring During Simultaneous Discharge of Iron and Tungsten Ions. Z. A. Solovyeva and A. T. Vagramyan	185	230
5. Reaction of Vitreous Sodium Silicates and Aluminosilicates with Aqueous Solutions. Communication 2. Reaction of Vitreous Sodium Disilicate with Aqueous Solutions. Yu. A. Shmidt	191	236
6. Reaction of Vitreous Sodium Silicates and Aluminosilicates with Aqueous Solutions. Communication 3. Effect of the Addition of Silica and Alumina to Sodium Silicates on the Instability of the Latter to Acids. S. K. Dubrovo	197	244
Organic and Biological Chemistry		
7. Synthesis of Sulfur-Containing Polyhalo Compounds and of ω,ω'-Thiodicarboxylic Acids. A. N. Nesmeyanov, L. I. Zakharkin, and R. G. Petrova.	205	253
8. Some Reactions of 3,3,3- and 1,1,3-Trichloropropenes. A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost, and R. Kh. Freidlina	209	258
9. Determination of the Individual Hydrocarbon Composition of Gasolines by the Combination Method. Communication 2. Two Gasolines from Kazanbulak Petroleums. B. A. Kazansky, A. F. Plate, E. A. Mikhailova, A. L. Liberman, M. I. Batuev, T. F. Bulanova, and G. A. Tarasova	215	266
10. Determination of the Individual Hydrocarbon Composition of Gasolines by the Combination Method. Communication 3. Surakhan Gasolines. B. A. Kazansky, G. S. Landsberg, A. F. Plate, A. L. Liberman, E. A. Mikhailova, P. A. Bazhulin, M. I. Batuev, S. A. Ukholin, T. F. Bulanova, and G. A. Tarasova	225	278
11. Synthesis of Sulfur Compounds by the Aid of Vinyl Ethers and Acetylene. Communication 7. Peculiarities of the Reaction of Addition, Contrary to Markovnikov's Rule, of Hydrogen Sulfide to Butyl Vinyl Ether. M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro	235	292
12. Synthesis of Sulfur Compounds by the Aid of Vinyl Ethers and Acetylene. Communication 8. General Method for the Synthesis of 2-Alkoxyethanethiols. M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro	245	303
13. New Method for the Synthesis of Amino Phosphonic Acids. Communication 2. Reaction of Ketones with Dialkyl Phosphites and Ammonia. T. Ya. Medved and M. I. Kabachnik	255	314
14. Synthesis and Reactions of Vinyl Ethers of Ethanolamines. Communication 4. Copolymerization of 2-Vinyloxyethylamine with Methyl Methacrylate. M. F. Shostakovsky, I. A. Chekulaeva, and A. M. Khomutov	263	323
15. Stereochemistry of Cyclic Compounds. Communication 3. cis- and trans-4-Cyclohexene-1,2-Dicarboxylic Acids, and Their Reactions. I. N. Nazarov and V. F. Kucherov.	269	329
16. Hydrogenation and Dehydrogenation of Hydrocarbons in Presence of Ruthenium and Rhodium Catalysts of Low Metal Content. Kh. M. Minachev, N. I. Shuikin, and I. D. Rozhdestvenskaya	277	338

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OBITUARY

ACADEMICIAN VLADIMIR MIKHAILOVICH RODIONOV

The death occurred on February 7, 1954, of Academician Vladimir Mikhailovich Rodionov, the eminent chemist, great technologist, and teacher, one of the founders of our synthetic dye industry and of the industry concerned with the preparation of alkaloids and pharmaceuticals.

V. M. Rodionov was born in Moscow on October 16 (28, New Style), 1878; he was educated in Moscow, graduating from the Moscow Technical High School.

His scientific activities have been characterized by the profundity of the investigations that he and his numerous students have carried out and by the wideness and variety of his scientific interests. He has published more than 150 scientific papers and has received more than 15 Author's Certificates for inventions; he has translated and edited about twenty important books and monographs on various branches of chemistry. He has discovered and developed new methods for the alkylation of organic compounds that are widely applied in the pharmaceutics and dye industries, and he proposed an original method for the preparation of diazophenolsulfonic acids, which are of great importance in the preparation of high-quality dyes. He has discovered also, methods, remarkable for their simplicity, for the synthesis of β-amino acids, which are of very great importance in biology. Of no less importance are the methods developed by Rodionov for the conversion of β-amino acids and their derivatives into various types of heterocyclic compounds, which are widely used for the synthesis of medicinals, vitamins, and antibiotics.

In the course of his long career as a teacher, Rodionov trained hundreds of talented technologists and investigators, including many who are now occupying responsible posts in industry, in the higher-teaching establishments, and in the research institutes; some of his students have already established their own schools of investigation and have opened up new fields of work. More than thirty of his students are doctors of science, and more than seventy are candidates of science.

In addition to his scientific and teaching activities, Rodionov did much organizational work: he occupied a number of responsible positions in industry, and in the later years of his life he was president of the Technical Council of the Ministry of Chemical Industry.

V. M. Rodionov was a very significant figure in Soviet chemical circles. For many years he occupied responsible positions in the D. I. Mendeleev All-Union Chemical Society, and in his later years he was president of this society.

In 1939 he was elected a corresponding member of the USSR Academy of Sciences, and in 1943 he became an academician.

The Soviet government greatly appreciated Rodionov's services to his Fatherland, and he was awarded three Stalin prizes, the Order of Lenin, two Orders of the Red Banner of Labor, and a medal "For Valiant Work in the Great Patriotic War, 1941-1945".

In the loss of V. M. Rodionov, Soviet science has suffered a great blow. Scientists, industrial workers, and students will long retain vivid memories of Vladimir Mikhailovich Rodionov, as a great scientist, fervent patriot, and remarkable man.

Presidium of the USSR Academy of Sciences; Division of Chemical Sciences of the USSR Academy of Sciences; Ministry of Culture of the USSR; Ministry of Chemical Industry of the USSR; Ministry of Health of the USSR; D. I. Mendeleev All-Union Chemical Society.

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REACTIONS OF PHENOL WITH PHOSPHORUS

S. I. Volfkovich, V. K. Kuskov, and K. F. Koroteeva

As is well known, white and red phosphorus react with water at high temperature and under pressure, and various compounds are produced according to the conditions under which the reaction is carried out. When water vapor reacts with heated phosphorus, phosphorous acid and phosphine are formed [1], and when phosphorus and water react under pressure, phosphoric acid and hydrogen are formed [2], together with smaller amounts of other products. With aqueous solutions of caustic alkali, white phosphorus gives mainly hypophosphites and phosphine, and the same reaction occurs with red phosphorus at 130-170° under pressure.

In 1906 Berthaud [3] showed that the action of methanol and of ethanol on phosphorus is analogous to that of water: in a sealed tube at 250° or higher, alkylphosphonic and alkylphosphonous acids, alkylphosphines, phosphonium salts, and inorganic phosphorus compounds are formed. In 1907 Senderens [4] found that in presence of red phosphorus intramolecular dehydration of ethanol occurs. We have repeated Berthaud's reaction of phosphorus with ethanol in an autoclave at 240-250° under 100 atm, and have obtained a mixture of phosphorus-containing products, including products of b.p. 110-220°, the structures of which have not been established. The gaseous reaction products included ethylene, formed evidently by Senderens' reaction. The total yield of phosphorus-containing products was very small. When the reaction temperature was raised, decomposition products were obtained in appreciable amounts. A comparison of results described in the literature with our observations suggests that first of all dehydration of the alcohol occurs. The water formed by this reaction then reacts with phosphorus, and the molecules, ions, or radicals formed react with the alcohol, yielding various organic and inorganic phosphorus compounds. It is thus considered that the formation of these phosphorus compounds is the result of secondary reactions.

In the present investigation, we have studied the reaction of phosphorus with phenol, i.e., with an alcohol that is unable to undergo intramolecular dehydration. It was found that phenol does not react with red phosphorus, even at 300° in an autoclave. When a mixture of phenol, phosphorus, and a small amount of water is heated in an autoclave, a reaction sets in already at 200°: the pressure begins to rise rapidly and, irrespective of temperature and ratio of reactants, it attains 40-150 atm. From the products of this reaction, apart from unchanged phenol and the usual reaction products obtained from phosphorus and water (phosphoric and phosphorous acids, hydrogen, and phosphine), we have isolated phenylphosphine, diphenylphosphine, triphenyl phosphate, and also a water-soluble phosphorus-containing compound, which was considered to be phenylphosphonic acid, although it was not found possible to isolate this substance in an analytically pure state.

When phosphorus reacts with a mixture of phenol and sodium or potassium phenoxide in absence of water, reaction proceeds at 270°, and the pressure attains 56 atm. The main reaction product is diphenyl ether, and only qualitative indications of the presence of phosphorus-containing compounds were obtained. Reaction between phenol and phenoxide evidently occurs (intermolecular dehydration of phenol in presence of phenoxide as catalyst). The formation of traces of phosphorus compounds is evidently due to the action of phosphorus on water formed in the intermolecular condensation. When water is added, the reaction occurs even at 150°, and from the reaction mixture, apart from inorganic phosphorus compounds and unchanged phenol, phenylphosphine, triphenyl phosphate, and phenylphosphonic acid (contaminated with phosphates) may be isolated. Thus, when phosphorus reacts with phenol and a phenoxide in presence of water, a dismutation reaction occurs, probably by a chain mechanism analogous to that found in the reaction of phosphorus with water and aqueous solutions of alkalis; but, instead of inorganic phosphorus acids and phosphine, their phenylated analogs are obtained. Instead of phosphoric acid, therefore, triphenyl phosphate should be obtained, instead of phosphine — phenylphosphine, and finally, instead of phosphorous acid (or phosphites, such as $HPO(ONa)_2$) phenylphosphonic acid or disodium phenylphosphonate might be expected to be formed. These organic substances were in fact obtained in our experiments.

In accordance with the above, the formation of the organophosphorus compounds may be described in terms

of classical structural theory by means of the following equations:

$$2P + 2H_2O + 6C_6H_5OH \longrightarrow 2(C_6H_5O)_3PO + 5H_2;$$

$$2P + 2H_2O + C_6H_5ONa \longrightarrow C_6H_5PH_2 + NaH_2PO_3;$$

$$2P + 2H_2O + C_6H_5ONa \longrightarrow PH_3 + C_6H_5PO(OH)(ONa);$$

$$2P + H_2O + 2C_6H_5ONa \longrightarrow C_6H_5PH_2 + C_6H_5PO(ONa)_2.$$

The process is, however, considerably more complicated, and these equations indicate only the result of the reaction, and not its mechanism. It may be noted that at above 250° red phosphorus was converted into black, whereas at below 250° partial transformation into white occurred.

EXPERIMENTAL

Reaction of Phenol with Phosphorus in Presence of Water

A carefully blended mixture of 23.5 g (0.25 mole) of phenol, 6.8 g (0.22 mole) of red phosphorus, and 4.5 ml (0.25 mole) of water was introduced into a vertical 50-ml autoclave, and was heated at 250-265° under a pressure of 110 atm for 4 hours 30 minutes. The autoclave was set aside for twelve hours to cool, and the pressure was then 20 atm. Analysis showed that the gaseous products contained 99.5% of hydrogen. The mixture was diluted with water, and unchanged red phosphorus was filtered off, washed with ether, and vacuum-dried (5 g). The aqueous filtrate and ether washings were heated in a bath to remove ether, and the residue was extracted three times with 50-ml portions of benzene. The benzene extract was dried with magnesium sulfate, the benzene was driven off, and the residue was vacuum-distilled at 3 mm. Fractions boiling at 87-96° and 170° were collected. The first fraction was 2.8 g (0.025 mole) of phenylphosphine, which was redistilled under atmospheric pressure (b.p. 160°).

Analysis (Marie's method)

Found %: P 27.63; 27.67

C_6H_7P. Calculated %: P 28.18

The second fraction was 1 g (0.062 mole) of diphenylphosphine, b.p. 272° at atmospheric pressure.

Found %: P 15.92; 15.84

$C_{12}H_{11}P$. Calculated %: P 16.6

Phenol was removed from the aqueous portion by steam distillation, and the residue was evaporated down. The solid residue was dried on a water bath and then in a vacuum desiccator over phosphoric oxide. The product was 4 g of a yellowish hygroscopic crystalline substance containing 16% P (Marie's method). Calculation for phenylphosphonic acid ($C_6H_7PO_3$) gives 19.6% P. The product contained carbon and hydrogen and gave the typical copper, iron, and barium salts of phenylphosphonic acid.

In another experiment in which half the amount of water was used (2.25 ml, i.e., 0.12 mole) (200°, 50 atm, 16 hours), an analogous treatment yielded diphenylphosphine and a mixture of phosphorous acids, as in the preceding experiment.

Reaction of Sodium Phenoxide with Phosphorus

a) In Presence of Water. A carefully blended mixture of 8.2 g (0.26 mole) of red phosphorus, 23.2 g (0.2 mole) of dry sodium phenoxide, and 3.6 g (0.2 mole) of water was introduced into the autoclave. The temperature was raised gradually to 250° over a period of four hours, when the pressure had attained 47 atm. This temperature was maintained for three hours, and the autoclave was allowed to cool over twelve hours, when the pressure became 30 atm; the gas present consisted of hydrogen and phosphine.

The gaseous products were released through a needle valve, and the mixture was extracted from the autoclave with 200 ml of hot water. The mixture was neutralized with hydrochloric acid, and unchanged phosphorus was filtered off under suction, washed with ether to remove organic substances, and dried. The phosphorus so obtained (4 g) was violet in color. The aqueous extract and ether washings were united and heated in a bath to remove ether. The oily layer that formed was extracted with benzene, and the extract was dried with magnesium sulfate and distilled. After removal of benzene and unchanged phenol, 0.7 g (0.0064 mole) of a colorless heavy oil having a characteristic phosphine odor came over under reduced pressure, b.p. 80-90° (3 mm); its boiling point at atmospheric pressure was 150-160°, which corresponds to phenylphosphine.

Phenol was steam-distilled from the aqueous layer, and the residue was evaporated until crystals appeared. The common salt was filtered off, and the residue was again evaporated until crystals appeared. The mixture was cooled, and the precipitate was filtered off and recrystallized from water, yielding 1 g of an organic substance that gave qualitative reactions for sodium phenylphosphonate: precipitates with copper sulfate (blue), ferric chloride (dark brown), and barium and calcium chlorides (white). When it was heated with zinc dust, there was a characteristic phosphine odor. Analysis for phosphorus, however, gave a value higher than that calculated:

Found %: P 17.05; 17.01

$C_6H_5PO_3Na_2$ Calculated %: P 15.2

The sodium phenylphosphonate obtained was apparently contaminated with sodium phosphate. The remaining filtrate was evaporated until crystallization occurred; cooling and filtration then yielded 1.4 g of disodium hydrogen phosphate.

When the amount of water taken was doubled (7.2 ml, i.e., 0.4 mole) (150° for 5 hours, 225° for 4 hours, 260° for 4 hours, and a maximum pressure of 60-90 atm), only traces of phosphines were obtained after a similar treatment, but distillation of the benzene extract yielded 1-2 g of triphenyl phosphate, b.p. 215° (4 mm) (colorless crystals, m.p. 48.5°). The literature gives m.p. 49-50°, b.p. 245° (11 mm).

Found %: P 9.26

$C_{18}H_{15}O_3P$. Calculated %: P 9.50

Hydrolysis of the product at the boil with 10% caustic soda solution for two hours gave phenol (positive reaction with bromine water and ferric chloride) and sodium phosphate (positive reaction with ammonium molybdate). In each of these experiments we obtained from the aqueous layer a phosphorus-containing organic substance, apparently impure phenylphosphonic acid, and about 5 g of a mixture of sodium phosphate and sodium phosphite.

b) In Absence of Water. A mixture of 13.5 g (0.09 mole) of sodium phenoxide, 17 g (0.18 mole) of phenol, and 3.96 g (0.12 mole) of red phosphorus was heated for two hours at 200° in an autoclave. The pressure attained 52 atm. The autoclave was heated further for one hour at 270°, and the pressure attained 56 atm. When the autoclave had cooled, the residual pressure was 30 atm. The gaseous products contained phosphine. The reaction mixture was treated as described above. Distillation of the benzene extract yielded 3 g of a substance of b.p. 160° (3 mm), and fractionation of this at atmospheric pressure yielded 2.3 g of a substance of b.p. 258°; qualitative tests indicated only carbon and hydrogen. The product corresponded in appearance, analysis, and boiling point to diphenyl ether.

Found %: C 83.8; H 6.35

$C_{12}H_{10}O$. Calculated %: C 84.4; H 5.9

The investigation has thus shown that it is possible to obtain aromatic organophosphorus compounds by the direct action of phenol or of a phenoxide on elementary phosphorus.

SUMMARY

1. When phenol, or a mixture of phenol and sodium phenoxide, is heated with red phosphorus under pressure and in presence of water, a mixture of phosphorus-containing organic compounds is obtained; it contains phenylphosphine, diphenylphosphine, and triphenyl phosphate.

2. When a mixture of phenol, sodium phenoxide, and red phosphorus is heated under pressure in absence of water, diphenyl ether and traces of organophosphorus compounds of unknown structure are obtained.

3. In absence of water, phenol does not react with red phosphorus, either at atmospheric pressure, or at elevated pressures.

4. A hypothesis is advanced concerning the nature of the reaction of phosphorus with phenol under the experimental conditions used.

Received June 28, 1953.

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COMPOUND OF HYDROGEN SULFIDE WITH PHENYLHYDRAZINE

B. A. Nikitin* and M. F. Pushlenkov

Compounds of inert gases with phenol and with toluene were first prepared by Nikitin [1] by the method of isomorphous coprecipitation. The compounds with phenol have the formula $A \cdot C_6H_5OH$, and those formed with toluene have the formula $A \cdot 2C_6H_5CH_3$, where A denotes an inert-gas atom. Later, a compound of radon and p-chlorophenol was obtained [2], and this had the formula $Rn \cdot 3ClC_6H_4OH$. These benzene derivatives form similar compounds with volatile hydrides, in particular, H_2S.

Terres and Vollmer [3] studied the melting point diagram of the phenol–hydrogen sulfide system, which indicated the presence of a molecular compound between hydrogen sulfide and phenol of the type $H_2S \cdot 2C_6H_5OH$. By means of a specially developed technique, we determined the melting point diagram of this system with greater accuracy [4], and we showed that the compound formed between phenol and H_2S has the formula $H_2S \cdot 3C_6H_5OH$. In investigations by Nikitin [5, 6, 7] it has been shown the most stable molecular compounds of the inert gases and their analogs, the volatile hydrides, are those formed with phenol.

We have now made a study of a benzene derivative, phenylhydrazine, with the object of preparing its compound with hydrogen sulfide. According to the literature [8], the compound of phenylhydrazine with hydrogen sulfide has the formula $H_2S \cdot C_6H_5NH \cdot NH_2$. However, the experimental procedure employed in this work [8] is open to some doubt, and so also, therefore, is the formula advanced for the compound. Although there was every indication that the compound was able to dissociate, the authors of this paper took no particular precautions and analyzed the compound obtained by the usual chemical method, a procedure that quite often leads to erroneous conclusions in such cases.

EXPERIMENTAL

The formation of the compound of phenylhydrazine with hydrogen sulfide was studied by the thermal-analysis method, the procedure being that already employed for analogous systems [4]. Since the system contains a volatile component, it was first necessary to obtain the temperature-pressure diagram (t-p) in order to permit a correction for the H_2S remaining in the gas phase to be made (in the calculation of the molecular ratio of components), when plotting the melting point diagram. The phenylhydrazine used in these investigations melted at $19.1 \pm 0.1°$; the hydrogen sulfide melted at $-85.0 \pm 0.3°$.

A weighed sample of phenylhydrazine was introduced into a glass ampoule, 1.0-1.5 ml in volume, which was then sealed to a mercury-in-glass monometer reading up to 8 atm (the other limb of the manometer was closed). Air was pumped from the apparatus via a side tube, the ampoule was cooled with liquid air, and H_2S was admitted from a buret graduated accurate within 0.1 ml. The side tube was then sealed off, so that the apparatus was hermetically closed (a small electromagnetic stirrer was introduced into the ampoule before it was sealed off). In order to establish the equilibrium pressure in the ampoule, this was kept for a long time at a definite temperature in a cryostat or thermostat that permitted direct observation to be made. During this time the liquid was vigorously and continuously stirred with the electromagnetic stirrer. When the equilibrium pressure was established in the vessel, it was recorded as the value for that particular temperature.**

The curve APH shows the variation of pressure with temperature for the equilibrium of three phases: solid phenlhydrazine, the liquid phase, and gaseous H_2S. The curve PMC corresponds to the case in which gaseous hydrogen sulfide, melt, and solid compound are in equilibrium. The curve DBP corresponds to the variation of the dissociation pressure of the solid compound (dissociating into solid phenylhydrazine and gaseous hydrogen sulfide); the section BP was determined experimentally, and the section DB was calculated (see below).

We give for comparison the curve EC, which shows the variation of the vapor pressure of H_2S over the liquefied gas with temperature. The section PH on the diagram corresponds to a metastable condition of three phases: solid phenylhydrazine, a solution of phenylhydrazine saturated with hydrogen sulfide, and gaseous H_2S. The intersection P (1.5°) of the curves APH and PMC corresponds to the upper eutectic point, at which four phases are in equilibrium:

* Deceased

** The results are listed in Table 1 and presented graphically in Fig. 1. The first 22 readings given in Table 1 correspond to the curve APH in Fig. 1, and the remaining readings correspond to PMC.

TABLE 1

Temp (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)
19.0	0.00	0.0	3.91	−14.0	5.48	−76.0	0.36
18.0	0.27	−1.0	3.96	−20.0	4.93	−80.0	0.27
		−3.0	4.08	−24.0	4.45	−81.0	0.24
17.0	0.71	−5.0	4.16	−26.0	4.12	−84.0	0.22
16.0	1.27			−28 0	3.88	−85.0	0.21
15.0	1.67	1.2	4.18	−30.0	3.62	−86.0	0.19
14.0	1.87	0.8	4.45	−32.0	3.36	−87.0	0.18
13.0	2.07	0.5	5.02	−34.0	3.12	−88.0	0.18
12.0	2.20	0.2	5.20	−36.0	2.70	−89.0	0.17
11.0	2.38	−1.0	5.70	−40.0	2.45	−90.0	0.16
10.0	2.78	−2.0	5.90	−44.0	2.12		
9.0	2.92	−3.0	5.92	−46.0	1.93		
8.0	3.05	−4.0	5.96	−50.0	1.60		
7.0	3.20	−5.0	6.00	−54.0	1.32		
6.0	3.30	−6.0	6.00	−58.0	1.09		
5.0	3.49	−7.0	5.98	−62.0	0.82		
4.0	3.60	−9.0	5.91	−66.0	0.65		
3.0	3.78	−11.0	5.80	−70.0	0.51		
2.0	3.86	−14.0	5.62	−74.0	0.40		

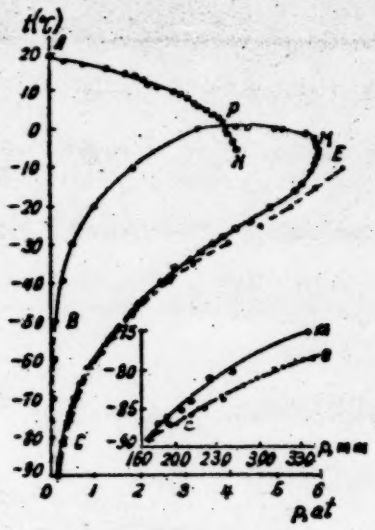

Fig. 1

solid phenylhydrazine, solid compound, melt, and gaseous H_2S. The point C on the t—p diagram corresponds to the lower eutectic point of the compound and solid H_2S (−87.5°). Thus, in the area DBPA we have solid phenylhydrazine and gaseous H_2S, and the area DBPMC corresponds to the simultaneous existence of solid compound and gaseous H_2S. It can be seen from this diagram that a compound is formed in this system having a maximum melting point of 1.5° at a maximum pressure of 6.0 atm.

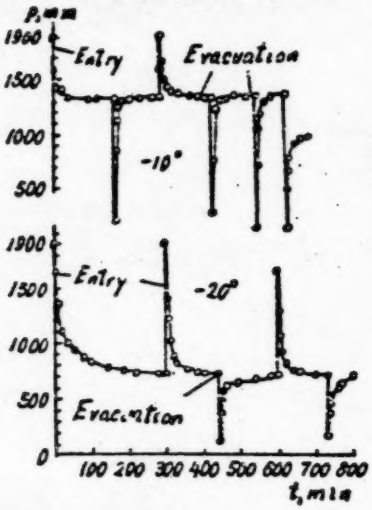

Fig. 2

In order to determine the dissociation pressure of the compound, a 6-8-g sample of phenylhydrazine was taken, cooled to −15.0°, ground to a powder without access of atmospheric moisture, and introduced into a 6-8-ml ampoule. The ampoule was immersed in liquid air and sealed to a graduated manometer. The vessel was then immersed in a cryostat, and hydrogen sulfide was passed into it. The vessel was held for periods at various temperatures until the first crystals of the compound appeared, after which the reaction went fairly quickly. When each fresh portion of hydrogen sulfide was admitted, the pressure rose, and then fell to a value that was definite and constant at the given temperature. It was found that, by continual admittance of fresh portions of hydrogen sulfide, the whole of the phenylhydrazine could be caused to react. When a sufficient amount of the compound had been formed and equilibrium pressure had been established, H_2S could be removed from the gas phase. The pressure in the vessel would then fall, and then, owing to the dissociation of the compound, it would rise to the equilibrium value, and this process could be repeated until the whole of the compound had been decomposed into phenylhydrazine and hydrogen sulfide. By way of example the course of the attainment of the equilibrium dissociation pressure following successive admittances and removals of H_2S is shown in Fig. 2 for experiments at −10° and −20°. In this way the dissociation pressure of the compound was determined at various temperatures; the results are given in Table 2.

On the basis of the results given in Table 2 (for temperatures from +1.4° to −50°), an empirical equation (Equation 1) was derived for the dependence of dissociation pressure on temperature; it permits the calculation of the

of the dissociation pressure accurate within ±3%.

$$\log p = \frac{A}{T} + B, \qquad (1)$$

in which p is the pressure (mm Hg), T is the absolute temperature, and A and B are constants, which are determined graphically.

TABLE 2

Dissociation pressure (mm Hg)	Calculated										
	2880	2510	1347	719	367	179	83	32	12	4	2
Temp. (°C)	1.4	0.0	−10	−20	−30	−40	−50	−60	−70	−80	−90

The experimental determination of the dissociation pressure of the compound at below −50° was practically impossible, because equilibrium is established very slowly at these temperatures. The dissociation pressure was, therefore, calculated from Equation 1. The dissociation pressure results are shown on the t–p diagram by the curve PBD, the section BD of which was calculated by Equation 1. Having determined the dissociation pressure of the compound at various temperatures below the eutectic point, it was possible to calculate the formation temperature of the compound by Clapeyron's equation, which may be transformed into the form

$$\log p = -\frac{Q}{2.303R} \cdot \frac{1}{T} + \text{const.} \qquad (2)$$

in which p is the dissociation pressure (mm Hg), Q is the heat of formation of the compound (cal/mole), T is the absolute temperature, and R is the gas constant.

We may find Q, therefore, by a comparison of Equations 1 and 2 (Q = 2.303RA), or graphically. The value of Q found in this way was 8500 cal/mole.

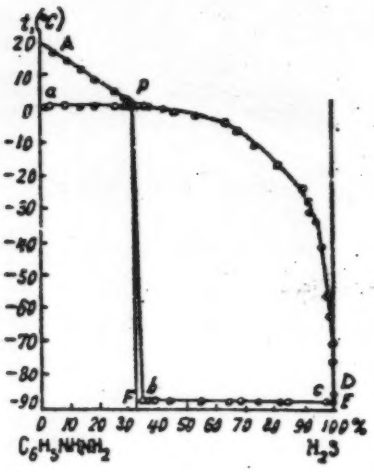

Fig. 3

Much supercooling occurs in the phenylhydrazine–H_2S system, and the determination of the melting point diagram by the temperature-arrest method is, therefore, not possible. The liquidus line was determined visually by observing the temperature at which the last crystal disappeared when the liquid was being stirred continuously. The solidus line was determined at temperatures close to the eutectic points by the centrifugation method developed previously [9].

The reaction vessel was a glass ampoule, volume 1.0-1.5 ml and having a ground joint at one end. A weighed amount of phenylhydrazine was introduced into the ampoule, and the electromagnetic stirrer was dropped in. The air was pumped out of the ampoule, and the required amount of H_2S was admitted by means of a tap attached at the ground joint. The H_2S was condensed, and the ampoule was sealed off while at the temperature of liquid air. The ampoule was then held at various temperatures in order to make sure that no compound was present. In the determination of the liquidus curve, the contents of the ampoule were heated until they melted, and were then frozen with liquid air; the ampoule was then immersed in a thermostat or cryostat (depending on the melting point). The ampoule was warmed slowly while its contents were stirred vigorously, and the temperature at which the last crystal disappeared was noted. The results of the experiments on the determination of the liquidus line are given in Table 3, and the melting point diagram in Fig. 3 was constructed from these results.

The liquidus line APCD consists of three curves: AP corresponds to the crystallization of pure phenylhydrazine, PC to the crystallization of the compound, and CD to the crystallization of H_2S. Two eutectic points were found on the liquidus curve: 1.4 ± 0.1° (33.3 mole% of H_2S) and −87.5 ± 0.3° (99.8 mole% H_2S).

The solidus line was determined on the sample used for the liquidus determination, or a new, similar sample was prepared.

TABLE 3

Ampoule No.	Mole-% of H_2S	Temp. of completion of melting (°C)	Ampoule No.	Mole-% of H_2S	Temp. of completion of melting (°C)
1	0.00	19.2			
2	4.80	17.4	2	3.50	+1.4
3	9.55	15.0	3	9.00	+1.4
4	14.56	12.7	4	14.20	+1.4
5	19.46	9.2	5	19.20	+1.4
6	26.20	5.8	6	26.10	+1.4
7	29.70	3.8	7	29.70	+1.4
8	31.23	3.0	9	31.20	+1.4
9	32.17	2.4	9	32.15	+1.4
10	32.50	2.0	10	32.70	+1.4
11	33.91	1.4	11	34.40	−87.5
12	34.76	1.2	12	35.10	−87.5
13	36.27	1.0	13	36.50	−87.5
14	38.44	0.8	14	39.10	−87.5
15	43.48	+0.2	15	44.00	−87.5
16	47.13	−0.2	16	54.80	−87.5
17	54.21	−2.0	17	64.40	−87.5
18	63.26	−6.2	18	68.30	−87.5
19	64.02	−7.6	19	74.00	−87.5
20	73.85	−10.5	20	81.50	−87.5
21	81.29	−16.8	21	94.40	−87.5
22	90.20	−24.0	22	96.10	−87.5
23	91.72	−28.0	23	99.00	−87.5
24	92.56	−31.0			
25	94.37	−33.5			
26	96.06	−41.0			
27	97.68	−54.5			
28	98.97	−62.0			
29	99.56	−70.5			
30	99.64	−75.5			
31	99.75	−85.5			
32	99.78	−87.5			
33	99.88	−86.0			
34	100.00	−85.0			

The contents of the ampoule were frozen, and were then placed in melting ice or chloroform, where the ampoule remained for 20 minutes It was then placed capillary downward in a centrifuge bucket filled with melting ice or chloroform (m.p. −63°), and was centrifuged for three minutes at 3000 r.p.m. The ampoule was then removed and examined for the presence or absence of liquid phase in the capillary. When liquid phase was present, the ampoule was immersed in the cryostat capillary downward; the liquid phase was then frozen and its melting point was determined. For systems poorer in hydrogen sulfide than the compound, liquid phase was absent after centrifugation at 0°; for systems richer in hydrogen sulfide, liquid phase was always to be observed. When liquid phase was absent, the ampoule was immersed in melting dimethylaniline, m.p. 2.0 ± 0.1°, and centrifuged while so immersed. After centrifugation, liquid phase was always to be observed in the capillary; this gave us reason to suppose that phenylhydrazine does not form a solid solution with H_2S. The ampoule was then placed in a cryostat, the liquid in the capillary was frozen, and the melting of the contents of the capillary was observed; they always melted at 1.4 ± 0.1° (for samples from No. 1 to No. 10). On the basis of these results the solidus line AP was constructed (Fig. 3); it passes between 0° and 2°, and corresponds to a temperature of 1.4 ± 0.1°.

In the experiments with ampoules No. 11 to No. 23, which were centrifuged at −63° (chloroform), the capillary always contained liquid phase, and this, when frozen, melted again at −87.5 ± 0.3°, which corresponds to the lower eutectic point on the melting point diagram. On the basis of these results, the solidus line bc, corresponding to this temperature, was constructed on the melting point diagram.

After the experiment the ampoule was opened and its volume was determined. The volumes of the stirrer and of the liquid or solid phase were subtracted from this volume. The amount of hydrogen sulfide remaining in the gas phase was calculated from the t−p diagram and this was subtracted from the amount taken for the experiment. Since the maximum pressure in the system did not exceed 6.0 atm, the correction for the volume of the gas phase was 2.0-2.5% with respect to the amount taken for the experiment. On the solidus line at 0° no liquid phase was to be observed up to 32.7 mole-% H_2S, and for 34.4 mole-% of H_2S and higher, liquid phase was absent at temperatures below −87.5°.

Although there is no clearly defined maximum on the liquid curve, the presence of a sharp drop in the solidus line from 1.4° to −87.5° over a range of 1.7 mole-% of H_2S proves that in the system

$$C_6H_5NH \cdot NH_2 - H_2S$$

a compound is formed between phenylhydrazine and H_2S. The line PbF, along which the system consists of one component (the compound), may be produced through the point P to the axis of abscissas to the point corresponding within experimental error to 33.3 mole-% of H_2S. The formula of the compound is therefore $H_2S \cdot 2C_6H_5NH \cdot NH_2$.

Knowing that H_2S is an analog of the inert gases, it might be expected that radon would be isomorphously coprecipitated with it, owing to the formation of an analogous compound with phenylhydrazine. In order to put this to the test, we carried out a series of experiments over a wide temperature range ($-10°$ to $-70°$), in which we studied the action of a gaseous mixture of hydrogen sulfide and radon on solid phenylhydrazine. It was established that radon does not enter into the compound, even in experiments in which 90% of the hydrogen sulfide taken reacts with phenylhydrazine with formation of $H_2S \cdot 2C_6H_5NH \cdot NH_2$.

In this case, therefore, H_2S cannot be regarded as an analog of the inert gases. The compound obtained, $H_2S \cdot 2C_6H_5NH \cdot NH_2$, cannot, therefore, be classed as a molecular compound formed by Van der Waals forces; it is more probable that it is to be classed as an ammonium compound of the type $(C_6H_5NH \cdot NH_3)_2S$, in which phenylhydrazine plays the part of ammonia.

SUMMARY

1. The melting point diagram of the system $C_6H_5NH \cdot NH_2 - H_2S$ has been determined by the method of thermal analysis. No clearly defined maximum has been found in the system. The curve for the composition passes through a transition point at which the maximum and eutectic point coincide and correspond to a composition of 33.3 mole-% of H_2S at $1.4 \pm 0.1°$, which is that required by the compound $(C_6H_5NH \cdot NH_2)_2S$.

2. The t–p diagram has been determined in the presence of three phases (solid, liquid, and gas), so that, when determining the melting point diagram, a correction could be introduced for the amount of volatile component remaining in the gas phase.

3. The dissociation pressure of the solid compound (dissociating into solid phenylhydrazine and gaseous H_2S) has been determined. At 0° the dissociation pressure is 3.3 atm, thus indicating the low stability of this compound.

The heat of formation of the compound from solid phenylhydrazine and gaseous H_2S has been determined from dissociation pressure data, the value obtained being 8500 cal/mole.

4. It has been shown that radon is not isomorphously coprecipitated with the compound formed by phenylhydrazine with H_2S and does not form an analogous compound with phenylhydrazine. The compound obtained, therefore, cannot be assigned to the class of molecular compounds, but must be regarded as an ammonium compound, i.e., of the type $(C_6H_5NH \cdot NH_3)_2S$.

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• See Consultants Bureau Translation, page 23.

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CONDITIONS FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF SILICIC ACID

COMMUNICATION 2. POLYMERIZATION OF SILICIC ACID

E. N. Egorova

Investigation of the procedure used in the dehydration method of separating silicic acid from solution has shown that separation of the acid by two dehydration treatments is not complete, even when optimum conditions are observed. The systematic discrepancies observed in parallel tests in the SiO_2 values found led to the supposition that the amount of silicic acid separated from solution depends not only on the dehydration conditions and the further treatment given to the precipitate, but also on the polymerization process to which the silicic acid has been subjected, prior to this treatment. If in the course of the evaporation of the acid solutions polymerization of silicic acid does not go to completion, then some of the silicic acid will remain in the form of simple nonpolymerized particles in the dry residue. During the further treatment of the dry residue and the dissolution of salts, this portion of nonpolymerized, or only slightly polymerized, silicic acid will again pass into solution.

The question of the polymerization of silicic acid arises also in connection with the completeness of its separation with the aid of coagulants in rapid methods of estimation. As would be expected, the completeness of the separation of silicic acid with the aid of coagulants depends on the extent to which the silicic acid passes into the colloidal state, i.e., on the extent to which polymerization occurs. This idea is not new: already in 1940 Weiss and Sieger [1] concluded that it is essential to give a prior treatment of the silicic acid in solution with concentrated solutions of mineral acids, in order to ensure that its conversion into the colloidal condition is as complete as possible before the coagulant is introduced.

The questions of the extent to which the polymerization of silicic acid in aqueous solution proceeds and of its reversibility have remained obscure. The published work on the polymerization of silicic acid has been carried out under conditions that do not correspond to those employed in its analytical determination, and this work is, therefore, not altogether applicable to the elucidation of the behavior of silicic acid in the course of analysis. Myllius and Groschuff [2] have investigated the polymerization of silicic acid in neutral solutions.

These authors obtained solutions of silicic acid by neutralizing solutions of sodium disilicate ($Na_2Si_2O_5$) with hydrochloric acid. The authors point out that, when the disilicate solution is rapidly neutralized with an equal volume of hydrochloric acid at 0°, the resulting neutral solution of silicic acid does not react with albumen; after long heating or standing, however, addition of albumen produces a turbidity.

When the disilicate solution is neutralized gradually, with heating after each addition of a fresh portion of hydrochloric acid, the resulting neutral solution forms a precipitate with albumen. Since silicic acid solutions that do not react with albumen acquire the ability to react after standing for a few days, these authors concluded that in neutral solution silicic acid is more stable in the form of polymers. On the basis of their investigations the authors divided silicic acids differing in degree of polymerization into two conventional groups: α- and β-silicic acids.

The concept of α-silicic acid introduced by these authors is a conventional one having only relative significance, for it relates to silicic acids of varying degree of polymerization, but having molecules that have not attained a sufficiently large size to be precipitable by albumen. The authors use the term β-silicic acid for the more highly polymerized forms, which are precipitated by albumen. The authors gave no indication of the limit of polymerization (i.e., degree of complexity) of α-silicic acid, but merely pointed out that the solutions that they obtained of the least complex silicic acids underwent polymerization in the course of time, and the rate of this reaction was increased by heating the solutions. Flemming [3] showed that the presence of small amounts of acids or alkalis in a silicic acid solution accelerates transition from true to colloidal solution.

Willstätter, Kraut, and Lobinger [4] studied the polymerization of silicic acid in hydrochloric acid solutions of pH 1-3.5. They prepared their silicic acid solution by the hydrolysis of silicon tetrachloride. Determination of the molecular weight of the silicic acid obtained by the cryoscopic method showed that it was present in the solution as disilicic acid.

When they neutralized the hydrochloric acid formed during the hydrolysis of silicon tetrachloride, the authors obtained silicic acid solutions, for which molecular weights corresponding to monosilicic acid were obtained. The pH stability regions were not identical for mono- and di-silicic acids: monosilicic acid was found to be most stable in solutions of pH 2-3, whereas disilicic acid was most stable at lower pH values, i.e., 1-2.

When solutions of the simplest acids are allowed to stand, their average molecular weight gradually rises and their diffusibility falls owing to the increase in the size and complexity of the molecules (formation of complex polymers). According to these authors the mean molecular weight of the silicic acid that reacts with albumen is higher than that of hexasilicic acid, and they introduce the idea of oligosilicic acids, by which term they describe silicic acids that are more complex than disilicic acid, but are not sufficiently complex to react with albumen. The oligosilicic acids are included in Myllius and Groschuff's α-silicic acid.

The results of the various investigations that we have cited indicate that the polymerization of silicic acid is a process that requires time and that increase in the acidity and temperature of the solution leads to an increased rate of polymerization. This process has not been subjected to quantitative investigation, and the question of the occurrence of kinetic equilibrium between the various forms of silicic acid remains obscure. There are some indications in the literature that such kinetic equilibrium may exist among the complex polymeric forms of silicic acid. Willstätter, Kraut, and Lobinger [5], for example, note that in silicic acid solutions, not only complex polymers may be present, but also more simple species. The occurrence of interconversion of one form into another is indicated by the work of Berestneva, Koretskaya, and Kargin [6], who investigated silicic acid sols by means of the electron microscope.

The question of the reversibility of the polymerization of silicic acid is of fundamental importance for its analytical determination. A study of the conditions favoring displacement of the equilibrium between the silicic acid polymers is, therefore, essential in order that an objective appraisal may be made of existing analytical procedures for the determination of silicic acid.

EXPERIMENTAL

Analytical and Experimental Procedure

In our study of the polymerization of silicic acid we have carried out a series of experiments with the object of elucidating the effect of the nature and concentration of the mineral acid, of the presence of salts, and of the duration of heating on the process. We have studied the course of the polymerization under given conditions by means of quantitative determination of the different forms of silicic acid present in the solution.

It is known that colloidal solutions of silicic acid do not react with molybdic acid with formation of the silicomolybdate complex. By the colorimetric method, therefore, we can determine only the part of the silicic acid that is present as simple molecules (or at a very early stage of polymerization). It is known also that colloidal silicic acid may be readily coagulated by the addition of coagulants and can then be separated from solution by simple filtration. Experiment has shown that the amount of silicic acid found colorimetrically in a suitably treated solution and the amount separable by treatment with gelatin are not together equal to 100% of the total amount introduced into the solution. It follows, therefore, that a suitably treated solution contains not only molecules of simple structure that react with molybdic acid and complex particles that are coagulated by gelatin, but also forms of intermediate complexity: not simple enough to react with molybdic acid, and not sufficiently complex in structure to be coagulated by gelatin.

We therefore, distinguish the following forms of silicic acid, which we classify according to the complexity of their particles: 1) α-silicic acid — various silicic acids in the early stage of the polymerization process, able to react with molybdic acid with formation of the silicomolybdate complex; 2) β-silicic acid — silicic acids that no longer react with molybdic acid, but are not yet sufficiently highly polymerized to be coagulated by gelatin; 3) γ-silicic acid — highly polymerized forms of silicic acids in which the particles are of colloidal dimensions or approach colloidal particles in complexity of structure (i.e., silicic acid sols).

We can determine α- and γ-silicic acids directly, and the content of β-silicic acid may be determined from the difference between the amount of SiO_2 taken for the experiment and the sum of the values found for the α- and γ-acids.

All three forms of silicic acid are given in the tables that follow. Comparing our classification with that proposed by Myllius and Groschuff, we see that these authors distinguish only two forms of silicic acids on the basis of molecular complexity (α- and β-forms). Myllius and Groschuff's β-form corresponds to our γ-form, and their α-form is separated in our classification into α- and β-forms, the reagent for the α-form being molybdic acid. Willstätter,

Kraut, and Lobinger regard Myllius and Groschuff's α-silicic acid as consisting of mono-di-, and oligo-silicic acids, but they indicate no method for distinguishing experimentally between these forms.

We have investigated the polymerization of silicic acid in hydrochloric acid, nitric acid, and sulfuric acid solutions. The effect of the variation of the concentration of mineral acid was studied for acidities ranging from zero to 8 N. Over the same acidity range the effect of the presence of sodium salts on the character and rate of polymerization was investigated. The duration of heating was varied from 15 to 60 minutes.

All of the experiments described below were carried out with a standard solution of sodium silicate containing 4×10^{-3} g of SiO_2 in 1 ml of solution. The standard solution was prepared from 1 g of silica calcined to constant weight at 1100° (the purity of the silica was tested by treatment with hydrofluoric and sulfuric acids: the amount not rendered volatile by this treatment was 0.1%, and this impurity was allowed for when weighing the sample). The sample of silica was fused with five times its weight of sodium carbonate, the melt was dissolved in water, and the volume of solution was made up to 250 ml. Colorimetric determination of silicic acid in this solution showed that it was all present in the α-form. For each experiment, 20 ml of the standard solution was taken (80 mg of SiO_2). The required amount of acid was then added, and the volume of the solution was in all cases made up to 100 ml with distilled water. Heating was effected by means of boiling water: the flask containing the solution under investigation was fitted with a reflux condenser and immersed in a boiling water bath. The solution was heated for the required time and then cooled rapidly under the tap; 5 ml of solution was then taken by pipet for the colorimetric determination of silicic acid, which was based on the color of the yellow silicomolybdate complex.

The remaining solution (95 ml) was heated to 70°, and a solution of gelatin (5 ml of a 2% solution) was added. If a precipitate formed, it was allowed to settle for 10-15 minutes and then separated by filtration. The precipitate was washed on the filter with hot dilute acid (5:95), and the filter paper and precipitate were ashed and calcined at 1040-1060° to constant weight. The calcined silica was tested for purity by treatment with hydrofluoric and sulfuric acids.

Polymerization of Silicic Acid in Weakly Acid and Almost Neutral Solutions

The polymerization of silicic acid in weakly acid and almost neutral solutions prepared by addition of hydrochloric acid was investigated for pH values ranging from 7.8 to 1.2. The procedure differed from that described above in that test samples for the determination of α-silicic acid were taken during the heating process at definite intervals of time. At the end of the experiment gelatin was added to the solution in order to coagulate any γ-silicic acid that had formed, but in no case was any detected (except in the experiment in which sodium chloride was added). The 5-ml portions of solution taken for determination of the α-form were diluted in measuring flasks to 50 ml with water, and silica was determined colorimetrically in the solutions obtained. After these diluted solutions had stood for two hours, further silica determinations were made.

It was found (Table 1) that at pH 1.2 after heating for as long as two hours no polymerization of silicic acid was to be observed. The further determinations of silicic acid in the diluted solutions after standing for two hours at room temperature again revealed no polymerization. With increase in the pH of the solution (from 1.9 to 3.7) polymerization of silicic acid occurred during heating, reaching its maximum value in the first 15-30 minutes; with further heating the reverse process of depolymerization occurred, the more complex molecules being converted into simpler molecules that were able to react with molybdic acid. The further determination of silicic acid, carried out after two hours in dilute solution, also showed that in some cases reversible conversion of β- to α-form occurred.

TABLE 1

pH of solution	Amt. of α-silicic acid (% of orig. amt.) after heating for				Second determination of α-silicic acid (% of orig. amt.) after 2 hours' standing			
	15 mins.	30 mins.	1 hour	2 hours	15 mins.	30 mins.	1 hour	2 hours
1.2	102	101	102	102	100	101	101	101
1.9	80	91	89	94	82	81	92	98
3.05	91	80	89	95	–	–	–	–
3.2	93	99	101	100	91	92	96	100
3.5	81	93	97	100	90	97	98	–
3.7	92	102	101	102	102	102	101	102
7.8	54.6	50.6	44.4	50.0	59	56	48	53
7.4*	50.6	50	45.6	47.2	54	54	49	–

* Addition made of 3 g of NaCl per 100 ml of solution.

In almost neutral solutions (pH 7.8), the rate of polymerization was considerably greater: after 15 minutes' heating, almost one-half of the silicic acid present in solution had passed into the β-form and so did not react with molybdic acid and was not coagulated by gelatin. With further heating (30 minutes and one hour) polymerization continued, but the conversion of the α-form into the β-form was appreciably slower. With still further heating (two hours) the reverse process, conversion of β-form into α-form, i.e., depolymerization, was observed. The reverse process was observed also when dilute solutions were allowed to stand. The state of the system in these solutions is determined by the equilibrium $\alpha \rightleftharpoons \beta$.

The presence of appreciable amounts of sodium chloride in almost neutral solutions alters the character of the polymerization. The amount of the α-form to be found in the solution (after 15 minutes' heating) was again 50% of its initial value, but at the same time flocs of silicic acid formed in the solution. This indicated that the polymerization was going further: conversion of the β-form into the γ-form. In this case the state of the system is determined by the more complicated equilibrium $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$. In dilute solutions containing sodium chloride, after standing or prolonged heating, the reversible conversion of the β-form into the α-form was again observed.

In order to determine the part played by the anion in the polymerization of silicic acid, experiments were carried out with solutions containing varying amounts of sodium sulfate and sodium nitrate at pH 7.3-7.7 (Table 2).

TABLE 2

Expt. No.	Salt (concentration in g/100 ml)		pH of solution	Amt. of α-silicic acid (% of orig. amt.) after heating for				Second determination of α-silicic acid (% of orig. amt.) after 2 hours' standing			
				15 min.	30 min.	1 hour	2 hours	15 min.	30 min.	1 hour	2 hours
1	$NaNO_3$	0.68	7.3	57	52.5	44.4	47	58	56	49	56
2		3.0	7.7	44	44	47	47	50	47	48	49
3	Na_2SO_4	0.5	7.5	84	81	61	45	82	45	62	51
4		3.0	7.5	93	89	61	47	99	90	65	44

In experiments with sodium nitrate in low (Expt. 1) and moderate (Expt. 2) concentration, the character and rate of polymerization were similar to those found for sodium chloride additions. Also, in presence of appreciable amounts of sodium nitrate, the formation of flocs of silicic acid was observed already after 15 minutes' heating. In the solution containing sodium sulfate in low concentration (Expt. 3), the initial rate of polymerization was considerably lower than in chloride and nitrate solutions under similar conditions, and only after two hours did the content of the α-form fall to 45%, a value close to that found in chloride and nitrate solutions. The presence of appreciable amounts of sodium sulfate (Expt. 4) delayed the conversion of the α-form into the β-form to a still greater extent in the initial stages (15 and 30 minutes), but after two hours' heating the amount of the α-form fell to 47%. In this case no flocs of silicic acid were formed; the solution merely became opalescent. In a sulfate solution, therefore, the second stage of the polymerization ($\beta \longrightarrow \gamma$) begins only after long heating of the solution.

We consider that, when a solution of sodium silicate is neutralized, the silicic acid formed undergoes a process of polymerization:

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3;$$

$$nH_2SiO_3 = H_2m\ Si\ n\ O(2n + m) + (n - m)\ H_2O,$$

in which $\underline{m} < \underline{n}$, and the value of $\underline{n}$ rises as polymerization proceeds, i.e., the silicic acid molecules become larger and more complex.

Our results indicate that the polymerization of silicic acid is a reversible process. In presence of salts and with rise in temperature the equilibrium is displaced to the right, i.e., the formation of polymeric forms of silicic acid is facilitated. On the other hand, presence in the solution of small amounts of acid (pH 1) leads to displacement of the equilibrium to the left, i.e., promotes the reverse process, depolymerization.

Polymerization of Silicic Acid in Acid Solutions

Hydrochloric Acid Solutions. The effect of variation in the concentration of hydrochloric acid was investigated over the range 1.4 N to 8 N. The effect of the duration of heating on the polymerization was investigated for the times 15, 30, and 60 minutes. The results obtained are illustrated in Figures 1, 2, and 3. Each point on the graphs represents a mean value, obtained from the results of a number of parallel experiments. The divergence between the values found in parallel experiments for the contents of α- and γ-silicic acids did not generally exceed 1-2%;

cases in which lower reproducibility was found are given special mention in the text.

From these results it will be seen that after 15 minutes' heating (Fig. 1), no polymerization is to be observed in a solution containing 5% HCl* (1.37 N); colorimetric determination shows that the whole of the silicic acid in the solution is present in the α-form. Even at an acidity of 2 N, practically no polymerization is to be observed under these conditions of heating.

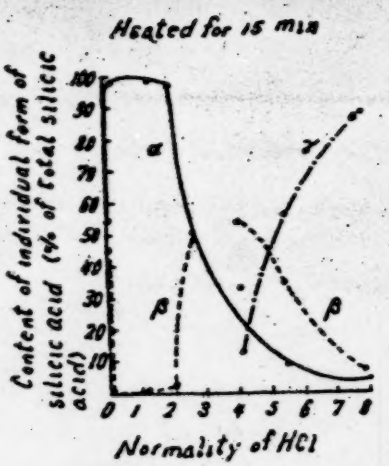

Fig. 1

When the concentration of HCl is increased to 10% (2.7 N), already after 15 minutes' heating only 50% of the initial amount of acid is in the α-form; the remainder is in the form of larger molecules, but these have still not attained sufficiently large dimensions to be coagulated by gelatin. In this case the state of the system is determined by the equilibrium $\alpha \rightleftharpoons \beta$. The divergence between the amounts of α-form found in parallel experiments is 5% (48% and 53%); this indicates an unstable state of equilibrium between α- and β-forms.

When the concentration of HCl is further increased to 15% (4 N), only 33% remains of the simplest form of silicic acid, and at the same time a third form, γ-silicic acid, is found to be present. The rate of conversion of the β- into the γ-form is less than the rate of conversion of the α- into the β-form. The solution, therefore, contains an appreciable amount of the intermediate β-form. The state of the system has become more complex, being determined by the equilibrium between three forms: $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$.

When the concentration of HCl is still further increased, the contents of α- and β-forms fall, and that of the γ-form rises. At 30% HCl (8 N), the mean value for the content of α-form is 4%, and the main form present is γ-silicic acid. We must point out that for this HCl concentration, whereas repeat experiments show satisfactory reproducibility for the α-form, a considerable variation is found for the γ-form (76.7-94.5%), which is reflected in the figures obtained, by difference, for the β-form. This indicates high lability in the equilibrium between β- and γ-forms and indefiniteness in the boundary between these forms.

Longer heating under the same conditions (30 minutes' heating; Fig. 2) results in practically no polymerization at relatively low concentrations of HCl, as in the case of the 15-minute experiments. When the concentration of HCl

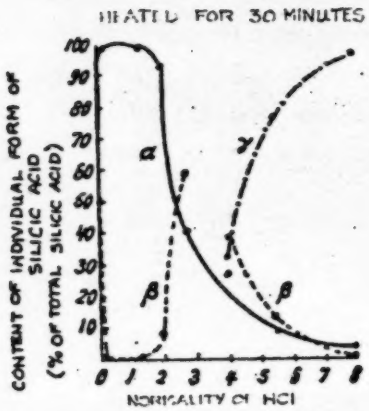

Fig. 2

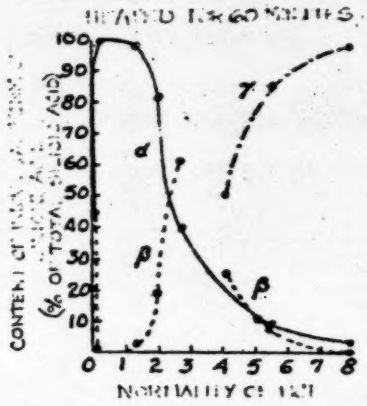

Fig. 3

is increased, the polymerization goes further than in the corresponding experiments at the shorter time of heating. Hence, when the duration of heating is increased, other conditions remaining constant, the equilibrium is displaced

* Here and later the concentration of acid is expressed in grams per 100 ml of solution.

in the direction of the formation of more complex particles. At HCl concentrations of 15% and higher, γ-silicic acid makes its appearance. At 20% HCl the content of the γ-form increases sharply, but the values found are poorly reproducible. At 30% HCl the results for the determination of α- and γ-forms are highly reproducible, indicating the stability of the equilibrium under these conditions, but the β-form is almost absent, and the system is, therefore, characterized by the equilibrium $\alpha \rightleftharpoons \gamma$.

With further increase in the duration of heating (Fig. 3), essentially the same picture is presented. The equilibrium $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$ is displaced somewhat more in the direction of the formation of more higly polymeric forms. The appearance of the γ-form is observed already at 10% HCl, for the solution becomes opalescent when gelatin is added.

Hydrochloric Acid Solutions containing an Appreciable Amount of a Salt (Sodium Chloride or Aluminum Chloride). In the series of experiments described above, the solutions contained only small amounts of sodium salts, formed when the original solution was acidified. Special experiments were carried out under the same conditions with the aim of determining the effect of large amounts of NaCl (up to 3 g per 100 ml) and of $AlCl_3$ (up to 80 mg per 100 ml). The results are given in Table 3.

TABLE 3

Concentration of HCl		Amount of various forms of silicic acid (% of total amount) after heating solution for 30 minutes								
					in presence of NaCl			in presence of $AlCl_3$		
(N)	(g/100 ml)	α	β	γ	α	β	γ	α	β	γ
0	0	50.6	49.4	–	50	–	–			
1.37	5	97.5			98.1			93.8		
		100.0	1.2	–	95.6	3.2	–	96.2	5	–
		98.8			96.8			95		
		40.0			38.8			42.5		
2.74	10	41.2	59.4		37.5	61.9	–	38.8	59.4	–
		40.6			38.1			40.6		
							64.6	9.4		67.0
							76.0	10.0		72.3
		9.7		71.3	8.8		74.0	9.7		72.1
5.48	20	9.4	14.6	80.4	8.1	18.8	71.7	8.8	20.3	70.2
		9.5		75.9	10.9		71.6	9.5		
					10.6					
					9.6					
		3.3	0.3	96.4	3.7		92.5	3.1		95.3
8.22	30	2.5	0.7	96.8	3.1	3.5	93.7	3.1	1.1	96.0
		3.1		97.1	3.4		93.1			95.65
		3.0		96.8						

It will be seen from Table 3 that the introduction of NaCl or $AlCl_3$ is practically without effect in the first stage of polymerization. The second stage of polymerization, the conversion of the β- into the γ-form, appears to be somewhat retarded by the presence of salts: to a greater extent by NaCl than by $AlCl_3$. At 20% and 30% HCl, the content of γ-form is less when polymerization occurs in presence of salts.

The experimental material described gives a sufficiently clear quantitative characterization of the course of the polymerization of silicic acid in hydrochloric acid solutions within the studied range of concentrations and times of heating. The experiments have shown that at all of the given HCl concentrations a more or less stable equilibrium between the various forms of silicic acid is established in the course of time (Fig. 4). Almost neutral solutions are exceptional: in this case there is a rapid fall in the content of α-silicic acid to 50-54% of its initial value, and as the duration of heating is increased, a stable equilibrium between the α- and β-forms is not established (Fig. 4).

In very weakly acid solutions (pH 1.9-3.7), at first (after 15-30 minutes' heating) there is a relatively small fall in the content of α-form (to 80% of the initial value), but with further heating the reverse process of depolymerization prevails, and the content of α-form increases and approaches its initial value. At pH 1.2, i.e., in a more acid solution, no polymerization at all is to be observed, even after heating for two hours. When the acidity is still further

increased to 1.4 N, the picture remains almost unchanged: there is a very slight fall in the content of α-form with time. The acidity range 0.1-1.0 N must, therefore, be regarded as the most favorable for the stable existence of silicic acid in its simplest form (within the limits of the period of time studied).

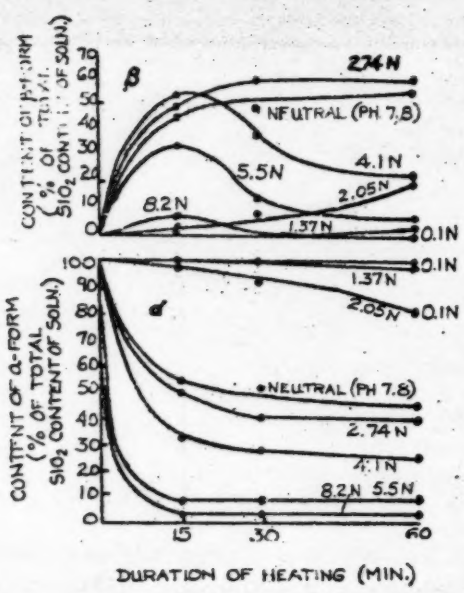

Fig. 4

Further increase in acidity beyond 1.4 N leads to polymerization of silicic acid, which becomes more and more pronounced as the acidity rises. This is shown by the rapid fall in the content of the α-form in the first period (15 minutes) of the heating, and by the slower fall in the further period of heating. In the acidity range 2-4 N, equilibrium between α- and β-forms is not attained during one hour's heating, although the curve for the variation of content of α-form with time becomes more and more nearly horizontal after 30 minutes' heating.

For acidities of 5.5-8 N the content of α-form is already much less after 15 minutes' heating, and then remains constant during further heating (parts of the curves that are parallel to the axis of abscissas). For acidities of less than 4 N the content of α-form is determined by the content of β-form. The curves for the variation of the contents of α- and β-forms with time form mirror images of one another: the equilibrium is determined by the concentrations of α- and β-forms. At acidities of greater than 4 N the content of β-form falls as it passes into the γ-form, and at 8 N the β-form is practically absent. The equilibrium of the system is apparently determined by equilibrium between simple and polymeric forms: $\alpha \rightleftharpoons \gamma$.

Nitric Acid Solutions. The effect of variation of the concentration of nitric acid on the polymerization of silicic acid was investigated over the same range of acidity, 0.8-8 N. The duration of heating was varied from 30 to 60 minutes. Also, the effect of sodium nitrate on the course of the polymerization process was examined under the same conditions. Comparison of the results (Figs. 5 and 6) with those obtained for hydrochloric acid solutions shows that in general character the processes are similar; nitric acid solutions, however, show a number of differences that are of interest.

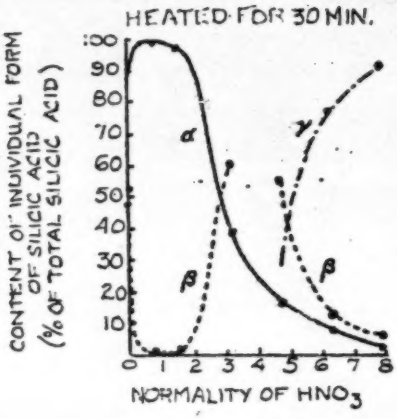

Fig. 5

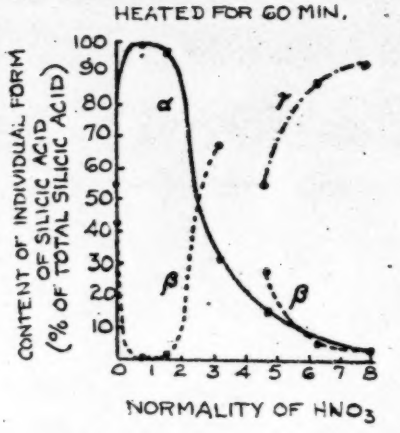

Fig. 6

1. In nitric acid solutions of medium concentration (3-4 N) the content of the α-form is somewhat greater after 30 minutes' heating than in hydrochloric acid solutions under the same conditions, i.e., the first stage of the polymerization, the conversion of the α-form into the β-form, proceeds somewhat more slowly; increase of the duration of heating to one hour reduces the difference. When the HNO_3 concentration is increased to 5 N this retardation of the first stage of the polymerization is no longer observed.

2. The second stage of the polymerization, the conversion of the β-form into the γ-form, is slower in nitric acid solutions, and in 8 N HNO_3 some β-form is still present, whereas in 8 N HCl it cannot be detected.

3. In general, the presence of sodium nitrate in nitric acid solutions has no effect on the polymerization of silicic acid, only in a definite range of acidity (4-5.5 N) does it retard the conversion of the β-form into the γ-form.

Sulfuric Acid Solutions. The effect of the variation of the concentration of sulfuric acid was investigated over the acidity range 1-8 N, heating being for 30 and 60 minutes. In addition, the effect of sodium sulfate was investigated for the same range of concentrations of sulfuric acid (Figs. 7 and 8). The general character of the polymerization of silicic acid in sulfuric acid solutions is the same as in hydrochloric acid solutions, the main difference being that the process is slower than in hydrochloric acid and nitric acid solutions. In 8 N H_2SO_4 10% of α-form remains after one hour's heating, whereas in hydrochloric and nitric acid solutions of the same normality only 3% of α-form is to be found. Correspondingly, the content of γ-form in 8 N H_2SO_4 is 90%, as against 97% in hydrochloric acid solution. These peculiarities of polymerization in sulfuric acid solutions are probably associated with the lower activity of hydrogen ions, in comparison with that found in nitric and hydrochloric acid solutions of the same normality.

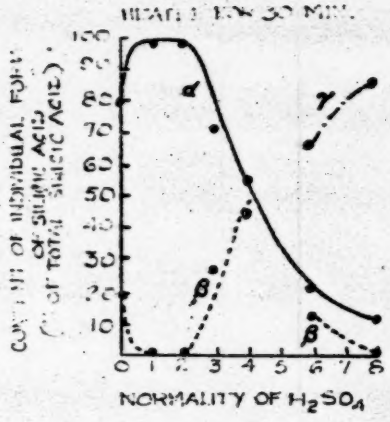

Fig. 7

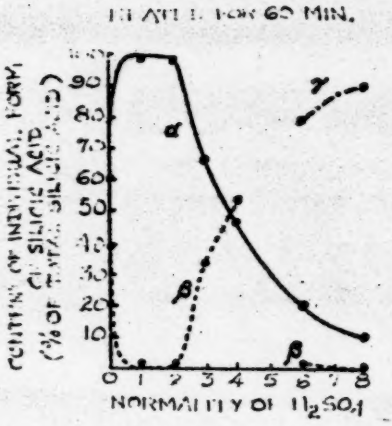

Fig. 8

SUMMARY

1. An investigation has been made of the dependence of the polymerization of silicic acid in aqueous solution on the concentration of mineral acid (HCl, HNO_3, H_2SO_4), on the content of certain salts in the solutions, and on the duration of the heating of the solution.

2. It is proposed that, in accordance with the complexity of their particles, three forms of silicic acid should be distinguished in aqueous solution: the simplest particles (α-form) react with molybdic acid, forming a colored complex; the most complex (γ-form) are coagulated by gelatin; and particles of the intermediate form (β-form) do not react with molybdic acid and are not coagulated by gelatin. This method of division has enabled the content of each of the three forms in a solution to be determined.

3. The laws determining the variation in the contents of these forms of silicic acid as the above-indicated factors are varied have been established. It has been shown that one form is reversibly convertible into another, and the conditions for the displacement of these equilibrium processes have been characterized.

4. The experimental material obtained and the regularities that it reveals are of practical interest for scientific development of methods for the separation of silicic acid from solutions.

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Institute of Silicate Chemistry of the USSR Academy of Sciences

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DISPLACEMENT OF CHEMICAL EQUILIBRIUM IN A SURFACE LAYER

S. E. Bresler and G. V. Samsonov

Chemical processes occurring at the boundary between two phases have been well studied from the point of view of kinetics: this study has formed the basis of a whole science—heterogeneous catalysis. Much attention has been paid also to the study of the kinetics of chemical processes occurring in insoluble films on liquid surfaces. The question of the equilibrium between substances reacting in the surface layer has not yet attracted attention; usually, the reactants and products, e.g., in heterogeneous catalysis, are found in the same phase, and therefore, from the point of view of thermodynamics, the course of the process in the surface layer has no effect on the composition of the final system.

The problem of the chemical processes occurring in a surface layer may be solved in a different way: by regarding substances remaining in boundary surface as products. The question then arises of the conditions of chemical equilibrium at the boundaries between phases. The experimental investigation of this question may be carried out with the aid of measurements of the physical properties of the reacting system or by a method depending on the "freezing" of the final products at low temperature, their transference into a homogeneous phase, and chemical analysis.

Our investigations on the course of chemical processes have been carried out in an insoluble film, formed on the surface of a liquid. It is well known from experiments with the Langmuir balance that the maximum lowering of surface tension in insoluble films is 30-40 dynes/cm. This lowering can be interpreted as a supplementary pressure created by the mono-layer on an area of length 1 cm and width equal to the length of the molecules oriented in the surface layer. It is easy to see, therefore, that the excess pressure in a surface layer may attain 200 or more atmospheres, sufficient to cause an appreciable displacement of chemical equilibrium in condensed systems, if the volume change in the chemical process is not too small and the free energy of the process is not too great. A favorable process from this point of view is the synthesis of esters from acids and alcohols. The esterification process should not occur in presence of the large mass of water in contact with the molecules of the surface layer, since water is produced in this reaction.

The free energy of the formation of esters from fatty acids and alcohols is $\Delta F = 900$ cal/mole [1]. The volume change during esterification in the surface layer is made up of two parts: the loss of water molecules and the formation of one large molecule from two small ones. Such processes should be accompanied by a volume change of not less than 20 ml per mole of ether. The associated external work $\Delta F' = p\Delta v$, which reduces the positive free energy of the chemical process, amounts to a few hundred calories. Under these conditions we might expect an appreciable displacement of the equilibrium in the surface layer, as compared with the homogeneous phase, in the direction of the synthesis of the ester. In addition, the orientation of the molecules in the surface layer and the resulting partial dehydration of the polar group may play an important part in the displacement of the chemical equilibrium. We may refer to this also as the effect of the steric factor: owing to the orientation of the ester molecules (when, as experiment shows, the area occupied by a molecule is 21 A^2 and the hydrocarbon radicals form, as it were, continuations of one another) the hydrophilic part of the molecule is removed from the aqueous phase, and this hinders the process of hydrolysis.

Both factors, therefore, displace the equilibrium in the surface layer in the same direction: from hydrolysis to esterification. Preliminary results on the formation of an ester in the surface layer from myristic acid and hexadecyl alcohol [2] were based only on the measurement of the fall in surface pressure after bringing a mixture of acid and alcohol onto the surface. In the present investigation we have made a systematic study of the process of esterification of various organic acids and alcohols both by the Langmuir-Adam method, and with the aid of microchemical colorimetric analysis.

EXPERIMENTAL PROCEDURE

The esterification process was studied for a series of organic acids—from lauric to palmitic—reacting with hexadecyl or octadecyl alcohol in monomolecular surface films formed on a water surface in a Langmuir trough. In carrying out the work all essential precautions were taken: the trough, covered with pure paraffin, was contained in a glass-covered box; two-way movement of the barrier was effected by remote control with the aid of nuts actuated

by a threaded rod attached to the wall of the box; the threaded rod was rotated by means of an electric motor, which was supported independently in order to avoid disturbance to the surface of the liquid. The surface tension (pressure) was measured by the detachment method, using a torsion balance and a glass plate having a perimeter of 20 mm. As all of the work was carried out with condensed films, a highly sensitive balance was not necessary. The probable error in the measurement of surface tension was 0.25 dyne/cm. For the formation of the film, a 0.1% solution of the acid and alcohol in hexane (distilled through a column) was used. The solution was applied in the form of 5-6 drops (total volume about 0.1 ml) from a specially calibrated micropipet. Removal of the film for analysis was carried out by two methods. transfer of the monomolecular layer to a solid metal plate [3], and decantation of the top layer of liquid, together with the film, into a special vessel. The first method gave the most reproducible results.

The esters formed in the films were extracted from the trough as described and subjected to chemical analysis. Since the total amount of acid and alcohol placed on the surface was only about 0.1 mg, and the amount of ester formed was still less, we selected the colorimetric method for the determination of esters by the hydroxamic reaction [4], which permits the determination of hundredths of a milligram of ester. The hydroxamic acid formed by the reaction of an ester and hydroxylamine in absolute ether

$$R_1COOR_2 + NH_2OH \rightarrow R_1CONHOH + R_2OH$$

gives a red complex with ferric salts:

$$3R_1CONHOH + FeCl_3 \rightarrow (R_1CONHO)_3Fe + 3HCl.$$

The extinction coefficients of the colored solutions were measured with a Soviet SF-1 spectrophotometer. The absorption curves of standard solutions of butyl oleate are given in Fig. 1. Fig. 2 shows the dependence of the extinction coefficient at 525 mμ on the concentration; it follows the Lambert-Beer law with great accuracy.

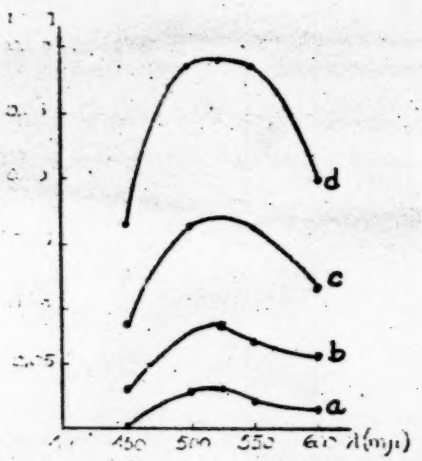

Fig. 1. Absorption curves for solutions of butyl oleate after formation of the hydroxamic complex: a) for $c = 0.185 \cdot 10^{-3}$ mM; b) for $c = 0.745 \cdot 10^{-3}$ mM; c) for $c = 1.78 \cdot 10^{-3}$ mM; d) for $c = 3.00 \cdot 10^{-3}$ mM

Our investigations have shown that the reproducibility of the results is not high when esters derived from acids having more than ten carbon atoms and alcohols of similar molecular size are analyzed by the method described. The presence of water in the ester solution has a considerable effect in these cases. Tolerable results can be obtained

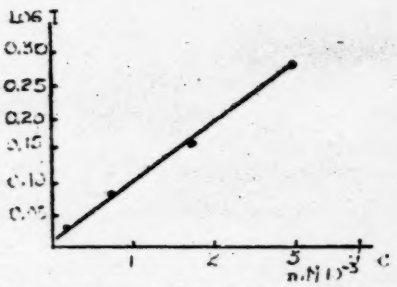

Fig. 2. Dependence of extinction coefficient on concentration.

only by long boiling of a solution of the ester and hydroxylamine in diethyl ether. The explanation of this difficulty may lie in the low solubility of the esters. For this reason we modified our procedure, carrying out the whole process of preparing the hydroxamic acid in absolute pentane, in which water is practically insoluble.

Results of the spectrophotometric investigation of the hydroxamic complex obtained from hexadecyl myristate in pentane are given in Figs. 3 and 4. The straight lines in Figs. 2 and 4 can be satisfactorily superposed, and this gives us reason to suppose that we may determine the concentration of any of the esters obtained from the same calibration curve when very high accuracy is not required. The hexadecyl myristate required for the construction of the calibration curve was synthesized by us from myristoyl chloride and hexadecyl alcohol and was recrystallized several times.

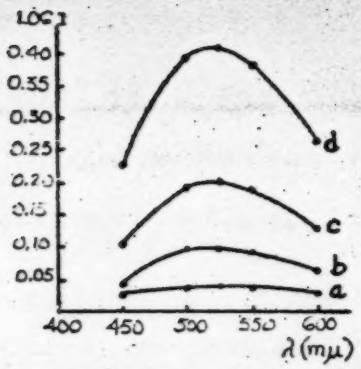

Fig. 3. Absorption curves for solutions of hexadecyl myristate after formation of the complex: a) for $c = 0.456 \cdot 10^{-3}$ mM; b) for $c = 1.14 \cdot 10^{-3}$ mM; c) for $c = 2.28 \cdot 10^{-3}$ mM; d) for $c = 4.56 \cdot 10^{-3}$.

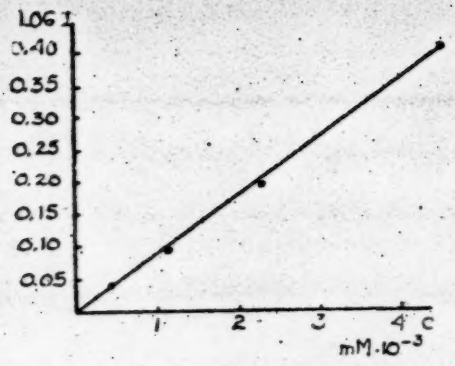

Fig. 4. Spectrophotometric curve for the hydroxamic complex formed from cetyl myristate in pentane.

Experiments on the Method of Determining Surface Pressure

The simplest method of observing chemical reactions in a surface layer covering a liquid is by measurement of the surface tension (surface pressure). We first studied the stability of films formed by the starting substances: lauric, tridecanoic, myristic, and palmitic acids, and hexadecyl and octadecyl alcohols. Films were formed with amounts of substance calculated to provide one molecule to each 25 A^2 of surface, and surface tension measurements were made at ten-minute intervals over a period of 3-5 hours. When films were formed on water, only the alcohols and palmitic acid gave fully stable films. When 0.02 N HCl was used, all of the films were found to be sufficiently stable with the exception of lauric and tridecanoic acid films. The acidity of the water phase reduced the dissociation of the fatty acids, and so reduced their solubility and stabilized the film. All further work was done on 0.02 N HCl. In the experiments on esterification, the amount of an equimolecular mixture of acid and alcohol necessary to provide one molecule for each 25 A^2 of surface was placed on the surface of 0.02 N HCl contained in the trough.

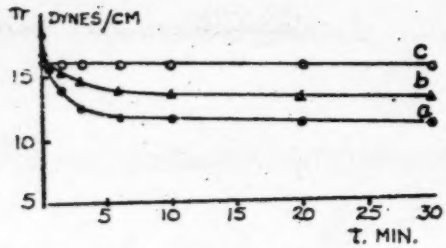

Fig. 5. Variation of surface pressure: a) myristic acid + hexadecyl alcohol; b) palmitic acid + hexadecyl alcohol; c) myristic acid + octadecyl alcohol.

The results of surface pressure measurements in the systems myristic acid + hexadecyl alcohol, palmitic acid + hexadecyl alcohol, amd myristic acid + octadecyl alcohol are given in Fig. 5. In the first and last systems there was an appreciable fall in surface pressure with time; it was substantially complete in one hour. No such effect was observed in the second system. We considered that palmitic acid formed a solid film at room temperature and could not react with the alcohol owing to the low mobility of its molecules. Experiments at 38° showed that under these conditions palmitic acid itself did not give a stable film owing to partial dissolution, so that a study of the kinetics of esterification could not be made from observations on the fall in surface pressure. However, synthesis of hexadecyl palmitate can be proved beyond doubt by means of chemical analysis.

Control experiments with surface films containing only acid or only alcohol showed (when stable films were obtained) that, when the substances were applied from hexane, the surface tension was established in 1-3 minutes, and then remained unchanged for several hours. As we considered that the surface pressure itself plays an important part in the displacement of chemical equilibrium, we carried out experiments in which we observed the change in surface pressure after compression and extension of the film, effected by movement of the barrier (Figs. 6 and 7). Both in the system myristic acid + hexadecyl alcohol and also in the system myristic acid + octadecyl alcohol, after each compression of the film (increase in surface pressure) a new gradual fall in surface pressure was observed, which occupied about ten minutes. After extension of the films the reverse phenomenon occurred: the surface pressure

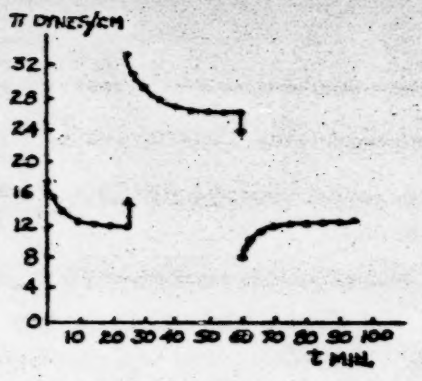

Fig. 6. Change in surface pressure after compression and extension of films in the system myristic acid + + hexadecyl alcohol.

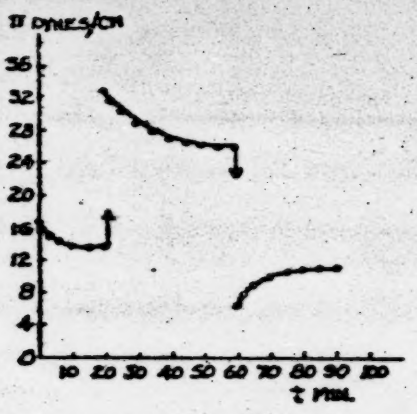

Fig. 7. Change in surface pressure after compression and extension of films in the system myristic acid + + octadecyl alcohol.

gradually rose. Our explanation of the observed phenomena is as follows: when the surface pressure is raised, further synthesis of ester occurs owing to a displacement in the equilibrium, and when the pressure is reduced the opposite process, ester hydrolysis, occurs. The control experiments with pure acids and alcohols indicated the insignificance of effects due to elastic after-effects, which cannot in any way eliminate the result obtained.

A study of the reverse process of ester hydrolysis, and particularly of the attainment of equilibrium from this side, would be of interest, but the films obtained by applying hexadecyl myristate to the surface of water were found to be fragile and of low stability: they exist for only a very short time and are broken down as soon as they are subjected to an insignificant pressure from the movable barrier. Experiments with hexadecyl myristate, and also with the ternary system myristic acid + hexadecyl alcohol + hexadecyl myristate, qualitatively confirmed our results on the existence of an equilibrium in this system in the surface film which is considerably displaced in the direction of ester synthesis. However, the low stability of the ester films did not allow us to obtain quantitative results.

Results of Chemical Analysis

Although there may still be some ambiguity in the interpretation of the observations on the change in surface pressure, the direct chemical analysis of the esters obtained shows beyond doubt that the chemical process does occur. As our preliminary results showed, the amount of ester obtained in one experiment from the whole of the trough (600 sq.cm) is insufficient even for an extremely sensitive method of colorimetric microanalysis. In order to obtain a larger amount of product, the film (formed from acid and alcohol and then maintained for 30 minutes) was compressed, and a glass plate having raised edges was introduced below it; the film, together with the top layer of liquid, was then transferred to a vessel contained in a Dewar flask containing liquid air (to freeze the equilibrium). This operation was repeated ten times for each system, and all the organic substances were then extracted from the water (after thawing) by means of pentane, and analysis for the content of ester was carried out by the hydroxamic method. The results of the spectrophotometric analysis of the hydroxamic complex in the systems lauric acid + hexadecyl alcohol, tridecanoic acid + hexadecyl alcohol, myristic acid + hexadecyl alcohol, and palmitic acid + hexadecyl alcohol (18° and 38°) are given in Fig. 8. The yield of ester in the surface layer may attain 20% (see Table).

The results obtained could only be convincing after numerous control experiments. With this object water films (0.02 N HCl), after remaining in the trough for a sufficient period of time, were analyzed in order to make sure that esters in micro amounts did not separate from the paraffin. Similar control experiments were carried out with films of fatty acids and alcohols. Each substance was separately applied to the surface of the solution in the trough. All these control experiments showed that the finding of ester in the synthesis experiments could not result from the contamination of the paraffin or the original acids and alcohols. There still remained the question of the possibility of the formation of esters after thawing of the pentane solutions. Experiments showed that mixtures of aliphatic alcohols and acids do not yield even traces of esters in the course of one day, when dissolved in pentane

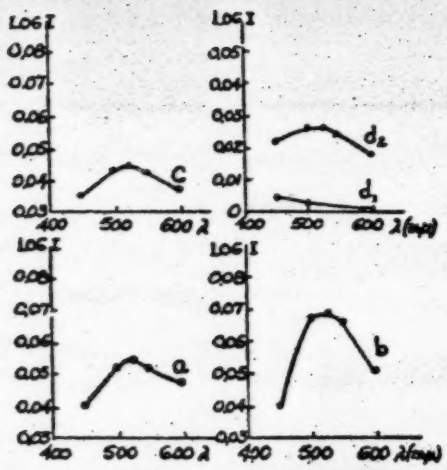

Fig. 8. Curves for the spectrophotometric investigation of the hydroxamic complex in the systems: a) myristic acid + hexadecyl alcohol; b) tridecanoic acid + hexadecyl alcohol; c) lauric acid + hexadecyl alcohol; d) palmitic acid + hexadecyl alcohol (d_1 at 18°, d_2 at 38°).

TABLE

Yields of Esters from Analytical Results

System	log I	Amount of ester (mM · 10^{-3})	Yield (%)
Myristic acid + + hexadecyl alcohol	0.055	0.64	16
Tridecanoic acid + hexadecyl alcohol .	0.069	0.80	20
Lauric acid + + hexadecyl alcohol	0.045	0.54	14
Palmitic acid + hexadecyl alcohol at 38° . . .	0.026	0.32	8

containing a small amount of acid (the pentane was first brought into equilibrium with 0.02 N HCl in a separating funnel).

This shows that not only the conditions for equilibrium, but also the rate at which equilibrium is attained, is different in the surface film than in the bulk of the solution, which, of course, is fairly well known to be so. The direct chemical experiment, therefore, was found to be in full accord with observations made by the Langmuir-Adam method. The occurrence of the synthesis of an ester from a fatty acid and an alcohol under the conditions existing in a monomolecular layer is proved. This proves also that under the conditions found in a monomolecular layer a dehydration reaction occurs in presence of a practically infinite reservoir of water; in other words, the peculiar conditions existing in the surface layer displace the chemical equilibrium from hydrolysis to synthesis.

SUMMARY

1. Esters have been synthesized from organic acids and alcohols in a monomolecular layer on the surface of water (0.02 N HCl). The formation of esters has been proved by a microchemical analytical method and also by the fall in surface pressure.

2. The synthesis occurs in presence of the enormous amount of water that supports the film. The possibility of the occurrence of the dehydration process is associated with the peculiar conditions that are found in the surface layer.

The effect of surface pressure on the displacement of chemical equilibrium in a monomolecular layer has been demonstrated.

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SYNTHESIS OF ω,ω,ω-TRICHLOROALKYLAMINES AND ω,ω-DICHLOROALKENYLAMINES

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No primary amines containing the trichloromethyl or 2,2-dichlorovinyl group and of the types $CCl_3(CH_2)_nNH_2$ and $CCl_2=CH(CH_2)_nNH_2$, are known. We decided to carry out the synthesis of such bifunctional compounds, since we considered that they should present considerable interest from the point of view of their reactivity, the mutual effect of the functional groups in the molecule, and so on [1, 2]. We hoped to effect the synthesis of compounds of these structures containing odd numbers of carbon atoms by the ammonolysis of α,α,α,ω-tetrachloroalkanes and α,α,ω-trichloroalkenes. α,α,α,ω-Tetrachloroalkanes are quite accessible substances, being prepared by the addition of carbon tetrachloride to ethylene with application of heat and pressure in presence of various initiators. Trichloroalkenes of structure $CCl_2=CH(CH_2)_nCl$ are readily prepared by the elimination of hydrogen chloride from these tetrachloroalkanes [3]. The synthesis of amines of the above types containing an even number of carbon atoms we hoped to bring about by the hydrogenation of nitriles, which would have to be obtained by the action of potassium or sodium cyanide on the corresponding tetrachloroalkanes or trichloroalkenes.

The action of ammonia on α,α,α,ω-tetrachloroalkanes has not been studied. It was thought that this reaction might be complicated by the fact that a highly nucleophilic reagent, such as ammonia, can attack the tetrachloroalkane molecule both at the carbon atom carrying one chlorine atom, and at the carbon atom carrying three chlorine atoms. Treatment of 1,1,1-trichloropentane with ammonia in a methanol medium at 145-150° for ten hours showed, however, that the trichloromethyl group is inert with respect to the action of ammonia under these conditions. 1,1,1,5-Tetrachloropentane, on being heated with ammonia in alcoholic solution, yielded 5,5,5-trichloropentylamine in satisfactory yield. 5,5-Dichloro-4-pentenylamine was formed as a by-product in this synthesis, and, in addition, resin formation occurred. The reaction between 1,1,1,7-tetrachloroheptane and ammonia did not go quite as well: the yield of the corresponding unsaturated amine approximated to that of 7,7,7-trichloroheptylamine, and there was also more resin formation. It was not found possible to obtain the trichlorononylamine from 1,1,1,9-tetrachlorononane and ammonia.

The reaction between α,α,ω-trichloroalkenes and ammonia went considerably better: it was found possible to obtain not only 5,5-dichloro-4-pentenylamine and 7,7-dichloro-6-heptenylamine, but also 9,9-dichloro-8-nonenylamine, the yields of the three substances being 73%, 56%, and 50% respectively.

The hydrogenation of nitriles containing a trichloromethyl or 2,2-dichlorovinyl group has not been studied. There is little information available also about the hydrogenation of other compounds containing the trichloromethyl group. We may, however, refer to a short communication [4] regarding the reduction of 1,1,1-trichloro-3-nitro-2-alkanols into the corresponding aminotrichloroalkanols by means of hydrogen in presence of Raney nickel in an absolute alcohol medium. Unfortunately, the authors have not published a more detailed paper on this subject. A patent [5] has appeared recently on the hydrogenation of polyhalo compounds containing a trichloromethyl group by means of hydrogen in presence of a platinum catalyst and a base for binding the hydrogen chloride formed. The reaction occurring under these conditions may be represented as follows:

$$2R-CCl_3 \xrightarrow[Pt]{H_2,\ NH_3} R-CCl_2-CCl_2-R \xrightarrow[Pt]{H_2,\ NH_3} RCH_2CH_2R,$$

where R is a hydrocarbon or halohydrocarbon residue.

By the hydrogenation of 6,6-dichloro-5-hexenenitrile under pressure in presence of Raney nickel in a methanol medium, the corresponding dichlorohexenylamine was isolated in low yield, and at the same time a small fraction of a lower-boiling fraction was obtained. It is possible that the low yield of product and the presence of

by-products are associated with the hydrogenation of the 2,2-dichlorovinyl group and with the replacement of a chlorine atom by hydrogen in presence of the base formed as a result of the hydrogenation of the cyano group. Carrying out the reaction under the same conditions, but in presence of 1,1,1,5-tetrachloropentane, which should act as a chlorine donor, led to the preparation of 6,6-dichloro-5-hexenylamine, and although a poor yield was obtained, there were no by-products, as the low-boiling substances were not formed under these conditions.

Hydrogenation of 6,6,6-trichlorohexanenitrile in a methanol medium in presence of Raney nickel led to the formation of 6,6-dichlorohexylamine, but not 6,6,6-trichlorohexylamine. We therefore carried out the synthesis of 6,6,6-trichlorohexylamine according to the following scheme:

$$CCl_3(CH_2)_4Cl + NaHC(COOC_2H_5)_2 \longrightarrow CCl_3(CH_2)_4CH(COOC_2H_5)_2 \xrightarrow[HCl]{H_2O} CCl_3(CH_2)_5COOH \xrightarrow{HN_3}$$

$$\longrightarrow CCl_3(CH_2)_5NH_2$$

All the amines that we have prepared are colorless liquids having a specific amine odor and distillable under reduced pressure. Trichloroalkylamines resinify appreciably on standing, and in the case of 5,5,5-trichloropentylamine, the hydrochloride of the original trichloropentylamine was isolated from the resinified mass. Dichloroalkylamines and dichloroalkenylamines are stable to storage. All the amines obtained form crystalline benzoyl derivatives when treated with benzoyl chloride. It is interesting to note that the benzoyl derivatives of the trichloroalkylamines containing an odd number of carbon atoms melt higher than the corresponding benzoyl derivative of the trichloroalkylamine containing an even number of carbon atoms. The same is observed also for the melting points of the benzoyl derivatives of the dichloroalkenylamines, as will be seen from the table.

TABLE

Benzoyl derivative	M.p. (°C)	Benzoyl derivative	M.p. (°C)
$CCl_3(CH_2)_4NHCOC_6H_5$	95-96	$CCl_2=CH(CH_2)_3NHCOC_6H_5$	55-56
$CCl_3(CH_2)_5NHCOC_6H_5$	70.5-71.5	$CCl_2=CH(CH_2)_4NHCOC_6H_5$	36-37.5
$CCl_3(CH_2)_6NHCOC_6H_5$	91-92	$CCl_2=CH(CH_2)_5NHCOC_6H_5$	37.5-38
		$CCl_2=CH(CH_2)_6NHCOC_6H_5$	—
		$CCl_2=CH(CH_2)_7NHCOC_6H_5$	44.5-45.5

EXPERIMENTAL

5,5-Dichloro-4-pentenylamine

A solution of 25 g of 1,1,5-trichloro-1-pentene in 100 ml of methanol containing 12 g of ammonia was heated in a steel ampoule at 80-85° for eight hours. The methanol and ammonia were then driven off in a water bath. Dilute hydrochloric acid was added to the residue, and the oil remaining undissolved was extracted with ether. The hydrochloric acid solution was cooled and made alkaline with a solution of caustic soda. The base that separated was extracted with ether, and the extract was dried with sodium sulfate. 5,5-Dichloro-4-pentenylamine (16.2 g, 73%) came over at 68-69° (7 mm); it had n_D^{20} 1.4899; d_4^{20} 1.1736; Found MR 37.98; Calculated MR 37.93.

	Found %:	N 9.22, 9.44
$C_5H_9Cl_2N$.	Calculated %:	N 9.09

Its benzoyl derivative melted at 55-56° (from ligroin).

	Found %:	N 5.50, 5.56
$C_{12}H_{13}Cl_2ON$.	Calculated %:	N 5.42

6,6-Dichloro-5-hexenenitrile

A mixture of 62 g of 1,1,5-trichloro-1-pentene, a solution of 32 g of potassium cyanide in 55 ml of water and 150 ml of ethanol, and 3 g of sodium iodide was heated with stirring for ten hours. The alcohol was then distilled off, and water was added to the residue to dissolve the salts. The oil present was extracted with chloroform, and the chloroform solution was washed once with water and dried with calcium chloride. Vacuum distillation yielded 13 g of the original trichloropentene and 42 g (72%) of 6,6-dichloro-5-hexenenitrile, b.p. 80-81° (3 mm), n_D^{20} 1.4815;

d_4^{20} 1.2018; Found MR 38.87; Calculated MR 38.99.

Found %: N 8.57, 8.34

$C_6H_7Cl_2N$. Calculated %: N 8.54

6,6-Dichloro-5-hexenylamine

A solution of 35 g of 6,6-dichloro-5-hexenenitrile and 35 g of 1,1,1,5-tetrachloropentane in 100 ml of methanol was hydrogenated in presence of 5 g of Raney nickel and hydrogen at 100 atm at 75° for three hours. After removal of the catalyst, the methanol was distilled off in a water bath. Dilute hydrochloric acid was added to the residue, and the undissolved part was extracted with chloroform. The hydrochloric acid solution was cooled and treated with a solution of caustic soda, when separation occurred of the free amine and also of nickel hydroxide, which had to be removed by filtration. The amine was extracted with ether, and the extract was dried with sodium sulfate. The dichlorohexenylamine (7.8 g, 22%) distilled over at 83-84° (6 mm); it had n_D^{20} 1.4865; d_4^{20} 1.1331; Found MR 42.61; Calculated MR 42.61.

Found %: N 8.56, 8.54

$C_6H_{11}Cl_2N$. Calculated %: N 8.33

Fractionation of the chloroform solution yielded 15 g of the original dichlorohexenenitrile. The dichlorohexenylamine, on being hydrolyzed with sulfuric acid, yielded 6-aminohexanoic acid, m.p. 200-201°, identified by determination of the melting point of a mixture of the substance with an authentic sample.

The benzoyl derivative melted at 36.5-37.5° (from ligroin).

Found %: N 5.08, 5.00

$C_{13}H_{15}Cl_2ON$. Calculated %: N 5.14

7,7-Dichloro-6-heptenylamine

1,1,7-Trichloro-1-heptene (12 g) was heated with 8 g of ammonia in 80 ml of methanol at 80-85° for eight hours. The residue after removal of methanol and ammonia was treated in the same way as in the case of 5,5-dichloro-4-pentenylamine. Vacuum distillation yielded 6.1 g (56.2%) of 7,7-dichloro-6-heptenylamine, b.p. 102-103° (7 mm); n_D^{20} 1.4842; d_4^{20} 1.1039; Found MR 47.19; Calculated MR 47.21.

Found %: N 7.52, 7.52

$C_7H_{13}Cl_2N$. Calculated %: N 7.69

The benzoyl derivative melted at 37.5-38° (from ligroin).

Found %: N 4.72, 4.97

$C_{14}H_{17}Cl_2NO$. Calculated %: N 4.89

9,9-Dichloro-8-nonenylamine

A solution of 23 g of 1,1,9-trichloro-1-nonene in 150 ml of methanol containing 15 g of ammonia was heated at 80-85° for ten hours. After removal of ammonia and methanol, the residue was treated in the same way as in the case of 5,5-dichloro-4-pentenylamine. Vacuum distillation yielded 10.6 g (50.5%) of the dichlorononenylamine, b.p. 100-101° (3 mm); n_D^{20} 1.4822; d_4^{20} 1.0599; Found MR 56.50; Calculated MR 56.45.

Found %: N 6.60, 6.75

$C_9H_{17}Cl_2N$. Calculated %: N 6.66

The benzoyl derivative melted at 44.5-45.5° (from ligroin).

Found %: N 4.56, 4.47

$C_{16}H_{21}Cl_2NO$. Calculated %: N 4.60

5,5,5-Trichloropentylamine

1,1,1,5-Tetrachloropentane (25 g) was heated in a steel ampoule with 20 g of ammonia and 100 ml of methanol at 85-90° for ten hours. The methanol and ammonia were driven off in a water bath. The crystalline residue was washed on the filter with chloroform, and then treated, with cooling, with a solution of caustic soda. The oil that separated was extracted with ether, and the ether extract was dried with sodium sulfate. Vacuum distillation of the product yielded 3.5 g of dichloropentenylamine and 13.2 g (58.2%) of trichloropentylamine; there was an appreciable residue in the distillation flask. The boiling point of 5,5,5-trichloropentylamine is 69-70° (1.2 mm);

n_D^{20} 1.4862; d_4^{20} 1.2619; Found MR 43.35; Calculated MR 43.21.

Found %: C 31.56, 31.60; H 5.31, 5.36; N 7.31, 7.33

$C_5H_{10}Cl_3N$. Calculated %: C 31.49; H 5.24; N 7.35

The benzoyl derivative melted at 95-96° (from aqueous alcohol).

Found %: N 4.70, 4.63

$C_{12}H_{14}Cl_3NO$. Calculated %: N 4.75

The hydrolysis of 5,5,5-trichloropentylamine with concentrated sulfuric acid yielded 5-aminovaleric acid, m.p. 155-156°. On standing 5,5,5-trichloropentylamine forms a precipitate of its hydrochloride, m.p. 229-230° (from water).

Found %: C 26.59, 26.64; H 4.98, 5.05; Cl 63.00, 62.90

$C_5H_{11}Cl_4N$. Calculated %: C 26.43; H 4.84; Cl 62.56

When the amine is heated above 130-140°, a vigorous reaction sets in with formation of hydrochloride and resins.

6,6,6-Trichlorohexanenitrile

A mixture of 63 g of 1,1,1,5-tetrachloropentane and a solution of 20 g of sodium cyanide and 3 g of sodium iodide in 150 ml of ethanol was heated with stirring for 10-12 hours. The alcohol was driven off in a water bath, and water was added to the residue to dissolve salts. The oil that was present was extracted with carbon tetrachloride, and the solution formed was dried with calcium chloride. Vacuum distillation yielded 8 g of the original tetrachloropentane and 48 g (80%) of 6,6,6-trichlorohexanenitrile, b.p. 91-92° (1.5 mm); n_D^{20} 1.4822; d_4^{20} 1.2877; Found MR 44.41; Calculated MR 44.33.

Found %: N 6.90, 7.08

$C_6H_8Cl_3N$. Calculated %: N 6.98

6,6-Dichlorohexylamine

6,6,6-Trichlorohexanenitrile (25 g) dissolved in 60 ml of methanol was hydrogenated in presence of 5 g of Raney nickel and hydrogen at 60-80°, 100 atm, for four hours. After removal of catalyst, the methanol was distilled off in a water bath. Dilute hydrochloric acid was added to the residue, and the undissolved oil was extracted with chloroform. The hydrochloric acid solution was rendered alkaline with caustic potash solution, cooling being applied. Separation occurred of the base and also of nickel hydroxide, which had to be removed by filtration. The amine was extracted with ether, and the ether extract was dried with potassium carbonate. Vacuum distillation of the product yielded a small first fraction (about 1 g) and 8.1 g of 6,6-dichlorohexylamine, b.p. 93-94° (7 mm); n_D^{20} 1.4730; d_4^{20} 1.1088; Found MR 43.01; Calculated MR 43.06.

Found %: N 8.12, 8.18

$C_6H_{13}Cl_2N$. Calculated %: N 8.23

From the chloroform solution, 7.2 g of uncharged nitrile was recovered.

The benzoyl derivative melted at 56-57° (from ligroin).

Found %: N 5.07, 5.05

$C_{13}H_{17}Cl_2NO$. Calculated %: N 5.11

The dichlorohexylamine underwent no change on being kept for a long time.

Diethyl 5,5,5-Trichloropentylmalonate

1,1,1,5-Tetrachloropentane (52 g) was added to sodiomalonic ester prepared in 60 ml of absolute ethanol from 32 g of malonic ester and 4.6 g of sodium. The solution was heated under reflux for eight hours, and then, to the cooled solution, water was added until the separation of oil was complete. The oil was extracted with chloroform, and the chloroform solution was dried over sodium sulfate. Vacuum distillation yielded 27 g of a first fraction, b.p. 76-140° (2.5 mm) and 43.1 g of diethyl 5,5,5-trichloropentylmalonate, b.p. 141-142.5° (2.5 mm); n_D^{20} 1.4624; d_4^{25} 1.2130. Found MR 75.64; Calculated MR 75.53.

Found %: C 43.70, 43.70; H 5.69, 5.76; Cl 31.34, 31.14

$C_{12}H_{19}Cl_3O_4$. Calculated %: C 43.20; H 5.69; Cl 31.92

7,7,7-Trichloroheptanoic Acid

A mixture of 43 g of the ester prepared as described above, 80 ml of glacial acetic acid, 50 ml of concentrated hydrochloric acid, and 60 ml of water was heated under reflux for ten hours. The acetic acid was then driven off under reduced pressure, and the oil remaining was extracted with chloroform. The residue after removal of solvent was heated at 170-180° until evolution of carbon dioxide ceased (30 minutes). When it had cooled, the product was dissolved in a slight excess of 10% aqueous caustic soda. The alkaline solution was extracted with ether and then acidified with hydrochloric acid. The trichloroheptanoic acid, which separated as an oil, was extracted with chloroform. Vacuum distillation yielded 22.5 g (73.5%) of 7,7,7-trichloroheptanoic acid, b.p. 120-121° (0.5 mm), m.p. 36-37° (from petroleum ether).

	Found %:	Cl 45.51, 45.48
$C_7H_{11}Cl_3O_2$.	Calculated %:	Cl 45.61

Hydrolysis of 7,7,7-trichloroheptanoic acid with concentrated hydrochloric acid gave a 92% yield of pimelic acid (m.p. 102-103°). The acid chloride of 7,7,7-trichloroheptanoic acid (b.p. 91-92°/1 mm) was obtained in almost quantitative yield by the action of thionyl chloride. The amide was prepared by the action of the acid chloride on aqueous ammonia, with cooling; m.p. 78-79°.

	Found %:	N 5.95, 6.04
$C_7H_{12}Cl_3ON$.	Calculated %:	N 6.02

6,6,6-Trichlorohexylamine

Concentrated sulfuric acid (40 ml) was added over a period of one hour at 40-45° to a solution of 20 g of 7,7,7-trichloroheptanoic acid in 60 ml of benzene containing 4.5 g of hydrazoic acid. The required temperature was maintained by means of external cooling. After the addition of the sulfuric acid the mixture was stirred for three hours further at the same temperature (until bubbles of gas ceased to separate). At the same time some hydrolysis of the trichloromethyl group was brought about by the sulfuric acid; it was for this reason that the temperature was not allowed to rise above 45°. When reaction was complete, the mixture was cooled and poured into ice water. The benzene layer was separated, and the sulfuric acid solution was carefully made alkaline (with cooling) by means of caustic soda solution. The oil that separated was extracted with ether, and the ether solution was dried with sodium sulfate. Vacuum distillation yielded 5.1 g (34.5%) of 6,6,6-trichlorohexylamine, b.p. 78-79° (1.2 mm); n_D^{20} 1.4843; d_4^{20} 1.2192; Found MR 48.01; Calculated MR 47.93.

	Found %:	N 6.85, 6.98
$C_6H_{12}Cl_3N$.	Calculated %:	N 6.84

The benzoyl derivative melted at 70.5-71.5°.

	Found %:	N 4.75, 4.60
$C_{13}H_{16}Cl_3NO$.	Calculated %:	N 4.53

7,7,7-Trichloroheptylamine

A solution of 30.5 g of 1,1,1,7-tetrachloroheptane in 150 ml of methanol containing 16 g of ammonia was heated in a steel ampoule at 85-90° for eight hours. The methanol and ammonia were driven off in a water bath, and the residue was treated as in the case of 5,5-dichloro-4-pentenylamine. Vacuum distillation of the product yielded 6.4 g of 7,7-dichloro-6-heptenylamine, b.p. 78-80° (1.5 mm) and 8.3 g (29.7%) of 7,7,7-trichloroheptylamine, b.p. 95-96° (1.5 mm). A considerable residue remained in the distillation flask, and this, on being heated, decomposed with evolution of hydrogen chloride. The trichloroheptylamine had n_D^{20} 1.4828; d_4^{20} 1.1857; Found MR 52.67; Calculated MR 52.55.

	Found %:	C 38.22, 38.40;	H 6.48, 6.44;	N 6.45
$C_7H_{14}Cl_3N$.	Calculated %:	C 38.44;	H 6.40;	N 6.40

The benzoyl derivative melted at 91-92° (from aqueous alcohol).

	Found %:	N 4.30, 4.45
$C_{14}H_{18}Cl_3NO$.	Calculated %:	N 4.34

SUMMARY

1. By the reaction of tetrachloroalkanes and trichloroalkenes having the structures $CCl_3(CH_2)_nCl$ and $CCl_2=CH(CH_2)_nCl$ with ammonia, the following amines have been prepared: $CCl_3(CH_2)_4NH_2$, $CCl_3(CH_2)_6NH_2$, $CCl_2=CH(CH_2)_3NH_2$, $CCl_2=CH(CH_2)_5\cdot NH_2$, $CCl_3=CH(CH_2)_7NH_2$, and their benzoyl derivatives.

2. Hydrogenation of polychloro nitriles of structure $CCl_3(CH_2)_4CN$ and $CCl_2=CH(CH_2)_2CN$ by means of hydrogen under pressure in presence of Raney nickel has yielded amines of structure: $CHCl_2(CH_2)_4NH_2$ and $CCl_2=CH(CH_2)_3NH_2$ and their benzoyl derivatives.

3. 6,6,6-Trichlorohexylamine has been prepared by the action of hydrazoic acid on 7,7,7-trichloroheptanoic acid. The trichloroheptanoic acid was prepared from 1,1,1,5-tetrachloropentane by the malonic ester synthesis. The acid chloride and amide of 7,7,7-trichloroheptanoic acid have been prepared.

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METHODS FOR THE PREPARATION OF MIXED ALKYL ORTHOTITANATES HAVING THE STRUCTURES $(RO)_3TiOR'$ and $(RO)_2Ti(OR')_2$

A. N. Nesmeyanov and O. V. Nogina

Among the organic compounds containing titanium, no compounds are known in which alkoxyl groups of more than one kind are present. Such compounds, however, are undoubtedly of interest from the point of view of reactivity and of their application for purposes of synthesis, particularly for the synthesis of titanoxane compounds. We considered that, of the possible methods of synthesis of mixed alkyl orthotitanates, the most promising were (a) the complete alkoxylation of alkoxyhalotitaniums of the type $(RO)_nTiX_{4-n}$, where n = 1, 2, 3, and (b) the action of titanium tetrachloride on a mixture of alcohols in presence of substances that will bind hydrogen chloride.

In titanium chemistry alcoholysis of the bond Ti – Cl is effected by the action of sodium alkoxides or of alcohols in presence of ammonia and amines. Having regard to our experience in working with alkyl orthotitanates, we decided to effect the synthesis of mixed alkyl orthotitanates by the action of alcohols on alkoxyhalotitaniums in presence of ammonia and amines in accordance with the equation:

$$(RO)_nTiX_{4-n} + (4-n)R'OH + R''_3N \longrightarrow (RO)_nTi(OR')_{4-n} + R''_3N \cdot HX.$$

The alkoxyhalotitaniums accessible at present are trialkoxychlorotitaniums [1] and alkoxytrichlorotitaniums [2]. With regard to dialkoxydichlorotitaniums, these are readily accessible only in the form of double compounds with alcohols [3, 4]. Their preparation free from alcohols presents some difficulties, and their use as starting materials for the synthesis of mixed esters of orthotitanic acid is therefore inconvenient.

The second method for the synthesis of mixed alkyl orthotitanates, which consists in the direct action of titanium tetrachloride on a mixture of alcohols in presence of ammonia and an amine is the simplest and most convenient, since it yields these compounds in one stage from very accessible starting substances. It is probable, however, that in the application of this method, a mixture of products will be obtained in a number of cases.

Study of the chemical properties of alkyl orthotitanates has shown that in the lower members the alkoxy groups are very mobile. They are, for example, very readily eliminated by the action of chlorine and bromine [4], and also, in a number of cases, by the action of pyridine hydrochloride [5]. The ready hydrolysis of alkyl orthotitanates points in the same direction [6]. It was to be expected, therefore, that it would be necessary to prepare mixed esters of orthotitanic acid under mild conditions in order to avoid their disproportionation, leading to the formation of a mixture of products, e. g. as follows:

$$4(RO)_3TiOR' \xrightarrow{\text{heat}} 3(RO)_4Ti + (R'O)_4Ti.$$

In view of these considerations we carried out the synthesis of mixed alkyl orthotitanates in the cold, distilled off the solvent at a pressure of 25-40 mm, and distilled off the esters at 1-2 mm; distilling only a small amount at a time.

We have studied the action of isopentyl alcohol on chlorotriethoxytitanium, of ethyl and isopentyl alcohols on chlorotripropoxytitanium, of ethyl, propyl, isopropyl, and allyl alcohols on chlorotriisopentyloxytitanium, of isopentyl alcohol on trichloro(2-methoxyethoxy)titanium, of hexyl alcohol on trichloroisobutoxytitanium, of isopropyl alcohol on trichloro(2-ethoxyethoxy)titanium, and of ethyl alcohol on trichloroisopentyloxytitanium. In some of the reactions ammonia was used to bind the hydrogen chloride, and in others pyridine and ammonia were

introduced successively into the reaction mixture [7]. In reactions performed in presence of ammonia and without addition of pyridine to the reaction mixture, it was not found possible to obtain completely pure mixed esters of orthotitanic acid. Analysis of the products gave carbon contents that were too high (by about 1%).

When the reactions were carried out in presence of pyridine with subsequent addition of ammonia, a number of mixed alkyl orthotitanates were obtained in the pure state. Thus, under these conditions it was found possible to effect the smooth, complete alkoxylation of alkoxychlorotitaniums by the action of primary alcohols (ethyl, propyl), secondary alcohols (isopropyl), primary alcohols having a branched chain (isopentyl), and unsaturated alcohols (allyl), the following esters were obtained: ethyl triisopentyl, triisopentyl isopropyl, isopentyl tripropyl, and allyl triisopentyl orthotitanates. All these substances are rather viscous, hygroscopic, readily hydrolyzable, colorless liquids, which can be vacuum-distilled. It must be pointed out that the thermal stability of the mixed alkyl orthotitanates varies greatly according to the nature of the alkoxyl groups present. Some of the substances obtained withstood two vacuum distillations, whereas others, already in the second distillation, boiled over a range of 15-20°.

In a number of cases we succeeded in obtaining mixed alkyl orthotitanates by the direct action of titanium tetrachloride on a mixture of alcohols in presence of pyridine and ammonia. In its general form, this reaction may be expressed as follows:

$$nROH + (4-n)R'OH + TiCl_4 + 4R_3^*N \longrightarrow (RO)_nTi(OR')_{4-n} + 4R_3^*N \cdot HCl.$$

When allyl and isopentyl alcohols were taken in a molar ratio of 1:3, allyl triisopentyl orthotitanate was obtained. When the alcohols were taken in equimolecular proportions, the reaction product was diallyl diisopentyl orthotitanate. Finally, when allyl and isopentyl alcohols were taken in the ratio 3:1, triallyl isopentyl orthotitanate was obtained. In each case the ester named was the sole reaction product.

It must be pointed out that the course of the reaction of a mixture of alcohols with titanium tetrachloride depends on the nature of the alcohols taken. Thus, by the action of titanium tetrachloride on an equimolecular mixture of isopentyl and propyl alcohols we obtained a 33% yield of isopentyl tripropyl orthotitanate, but no diisopentyl dipropyl orthotitanate.

The mixed alkyl orthotitanates prepared by this method were also viscous, hygroscopic, readily hydrolyzable liquids, which could be vacuum-distilled. The isopentyl tripropyl orthotitanate obtained by this method was found to be identical in all its properties with the substance obtained by the action of isopentyl alcohol on chlorotripropoxytitanium. In the same way the substances obtained by the action of allyl alcohol on chlorotriisopentyloxytitanium and by the action of titanium tetrachloride on a mixture of the corresponding alcohols were found to be identical.

EXPERIMENTAL

All of the experiments described below were carried out with carefully dried reactants under conditions that prevented access of atmospheric moisture to the apparatus.

Preparation of Mixed Alkyl Orthotitanates by the Action of Alcohols on Alkoxychlorotitaniums

Preparation of Triisopentyl Isopropyl Orthotitanate $i\text{-}C_3H_7OTi[OCH_2CH_2CH(CH_3)_2]_3$

A solution of 11.60 g (0.03 mole) of chlorotriisopentyloxytitanium in 60 ml of benzene was added slowly from a dropping funnel to a stirred, cooled (ice water) mixture of 2.00 g (0.03 mole) of isopropyl alcohol, 2.70 g (0.03 mole) of pyridine, and 60 ml of benzene contained in a three-necked flask fitted with mercury-sealed stirrer, dropping funnel, and reflux condenser. Ammonia was then passed into the flask for two hours. The precipitated pyridine hydrochloride and ammonium chloride were filtered off, and benzene and unchanged pyridine were distilled off at 25-30 mm. The triisopentyl isopropyl orthotitanate formed in the reaction was distilled off under reduced pressure; it came over at 154-155° (1.5 mm); n_D^{20} 1.4870; yield 65%.

	Found %:	C 58.60, 58.70; H 10.93, 11.19; Ti 13.00, 13.10
$C_3H_7OTi(OC_5H_{11})_3$.	Calculated %:	C 58.68; H 10.94; Ti 13.00

Preparation of Ethyl Triisopentyl Orthotitanate $C_2H_5OTi(OC_5H_{11}\text{-}i)_3$

The procedure of the previous experiment was followed, the substances taken for reaction being 2.00 g (0.043 mole) of ethyl alcohol, 3.40 g (0.043 mole) of pyridine, and 15.00 g (0.043 mole) of chlorotriisopentyloxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained after removal of benzene and unchanged pyridine distilled at 151-153° (2 mm); n_D^{20} 1.4910; yield of crude product 85%.

	Found %:	C 57.87, 58.14; H 11.06, 10.87; Ti 13.52, 13.54
$C_2H_5OTi(OC_5H_{11})_3$.	Calculated %:	C 57.61; H 10.80; Ti 13.51

Preparation of Allyl Triisopentyl Orthotitanate $CH_2 = CH - CH_2OTi(OC_5H_{11}\text{-}i)_3$

The same procedure was followed, the substances taken for reaction being 2.50 g (0.043 mole) of allyl alcohol, 3.40 g (0.043 mole) of pyridine, and 15.0 g (0.043 mole) of chlorotriisopentyloxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained distilled at 162.5-163.5° (1.5 mm); n_D^{20} 1.4960; yield of crude product 82%.

	Found %:	C 59.16, 58.85; H 10.65, 10.50; Ti 13.19, 13.07
$C_3H_5OTi(OC_5H_{11})_3$	Calculated %:	C 59.00; H 10.45; Ti 13.07

Preparation of Isopentyl Tripropyl Orthotitanate $(n\text{-}C_3H_7O)_3TiOC_5H_{11}\text{-}i$

The same procedure was followed, the substances taken for reaction being 4.06 g (0.046 mole) of isopentyl alcohol, 3.6 g (0.046 mole) of pyridine, and 12 g (0.046 mole) of chlorotripropoxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained distilled at 127-130° (1 mm); n_D^{20} 1.4950; yield 88%.

	Found %:	C 53.67, 53.92; H 10.38, 10.50; Ti 15.68, 15.74
$(C_3H_7O)_3TiOC_5H_{11}$	Calculated %:	C 53.84; H 10.33; Ti 15.33

Preparation of Triisopentyl Propyl Orthotitanate $n\text{-}C_3H_7OTi(OC_5H_{11}\text{-}i)_3$

The same procedure was followed, the substances taken for reaction being 2.10 g (0.034 mole) of propyl alcohol, 2.76 g (0.034 mole) of pyridine, and 12.26 g (0.035 mole) of chlorotriisopentyloxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained distilled at 149.5-151° (1.5-2 mm); n_D^{20} 1.4893; yield of crude product 98%.

	Found %:	C 59.11, 59.17; H 11.04, 10.87; Ti 12.89, 12.83
$C_3H_7OTi(OC_5H_{11})_3$.	Calculated %:	C 58.68; H 10.94; Ti 13.00

Preparation of Mixed Alkyl Orthotitanates by the Action of Titanium Tetrachloride on a Mixture of Alcohols

Preparation of Allyl Triisopentyl Orthotitanate $(i\text{-}C_5H_{11}O)_3TiOCH_2 - CH = CH_2$

A solution of 21.5 g (0.113 mole) of titanium tetrachloride in 60 ml of benzene was added slowly to a stirred and cooled (ice water) mixture of 30 g (0.340 mole) of isopentyl alcohol, 6.6 g (0.113 mole) of allyl alcohol, 35.9 g (0.45 mole) of pyridine, and 60 ml of benzene contained in a three-necked flask fitted with mercury-sealed stirrer, dropping funnel, and reflux condenser. When the whole of the titanium tetrachloride had been added, ammonia was passed for two hours. Precipitated pyridine hydrochloride and ammonium chloride were filtered off, and benzene and unchanged pyridine were distilled off at 25-35 mm. The residual viscous liquid all distilled over at 149-149.5° (0.5 mm). In a second distillation the substance distilled at 157.5-158° (1 mm); n_D^{20} 1.4960; yield of crude product 27.5 g (66%).

	Found %:	C 58.95, 58.94; H 10.60, 10.50; Ti 13.15, 13.24
$C_3H_5OTi(OC_5H_{11})_3$.	Calculated %:	C 59.00; H 10.45; Ti 13.07

Hence, in this experiment, the sole titanium-containing product obtained was allyl triisopentyl orthotitanate, identical in all its properties with the substance obtained by the action of allyl alcohol on chlorotripentyloxytitanium, as described above.

Preparation of Diallyl Diisopentyl Orthotitanate $(CH_2 = CH - CH_2O)_2Ti(OC_5H_{11}\text{-}i)_2$

The procedure of the preceding experiment was followed, the substances taken for reaction being 13.2 g (0.22 mole) of allyl alcohol, 20.0 g (0.22 mole) of isopentyl alcohol, 35.9 g (0.11 mole) of pyridine, and 21.6 g (0.11 mole) of titanium tetrachloride. Ammonia was passed into the reaction mixture for two hours. The diallyl diisopentyl orthotitanate obtained distilled at 160-161.5° (1 mm); n_D^{20} 1.5050; yield of crude product 77%.

	Found %:	C 57.41, 57.15; H 9.58, 9.86; Ti 14.49, 14.35
$(C_3H_5O)_2Ti(OC_5H_{11})_2$.	Calculated %:	C 57.14; H 9.59; Ti 14.24

Preparation of Triallyl Isopentyl Orthotitanate $(CH_2 = CH - CH_2O)_3TiOC_5H_{11}\text{-}i$

The same procedure was followed, the substances taken for reaction being 19.8 g (0.34 mole) of allyl alcohol, 10.0 g (0.11 mole) of isopentyl alcohol, 35.9 g (0.45 mole) of pyridine, and 91.6 g (0.11 mole) of titanium

tetrachloride. Ammonia was passed into the reaction mixture for two hours. The triallyl isopentyl orthotitanate obtained distilled at 150-151° (1 mm); n_D^{20} 1.5222; yield of crude product 27 g (77.5%).

	Found %:	C 54.45, 54.30; H 8.71, 8.68; Ti 15.74, 15.71
$(C_3H_5O)_3TiOC_5H_{11}$.	Calculated %:	C 54.90; H 8.56; Ti 15.64

In a second distillation the substance distilled over a wide range, 151-165° (1 mm), evidently owing to disproportionation of triallyl isopentyl orthotitanate, effected by heat.

Preparation of Isopentyl Tripropyl Orthotitanate $(n\text{-}C_3H_7O)_3TiOC_5H_{11}\text{-}i$

The same procedure was followed, the substances taken for reaction being 10.5 g (0.17 mole) of propyl alcohol, 15.5 g (0.17 mole) of isopentyl alcohol, 27.8 g (0.35 mole) of pyridine, and 16.7 g (0.088 mole) of titanium tetrachloride. Ammonia was passed into the reaction mixture for two hours. After removal of benzene and unchanged pyridine there remained 26.9 g of a viscous liquid, which corresponded to almost quantitative utilization of the mixture of alcohols taken. This liquid distilled over the range 152.5-164° (2 mm), and from the lower fraction in a second distillation a product b.p. 128-130° (1 mm) and n_D^{20} 1.4940, was isolated; it was identical in all of its properties with the isopentyl tripropyl orthotitanate obtained by the action of isopentyl alcohol on chlorotripropoxytitanium (see above). Analysis confirmed that the product had this composition.

	Found %:	C 54.25, 54.10; H 10.40, 10.48; Ti 14.80, 14.89
$(C_3H_7O)_3TiOC_5H_{11}$.	Calculated %:	C 53.84; H 10.33; Ti 15.33

The yield of pure isopentyl tripropyl orthotitanate was 33%, based on the amount of propyl alcohol taken. The higher-boiling fractions of the mixture of products obtained were not investigated further.

Disproportionation of Isopentyl Tripropyl Orthotitanate when Heated

Pure isopentyl tripropyl orthotitanate (5 g) from the preceding experiment was distilled under more severe conditions (6 mm). During distillation the substance underwent disproportionation, as evidenced by the fact that it distilled over the range 154-174°.

SUMMARY

1. A method for the synthesis of mixed alkyl orthotitanates has been developed: it consists in the action of alcohols on alkoxychlorotitaniums in presence of pyridine and ammonia.

2. Another method for the synthesis of mixed alkyl orthotitanates has been developed: it consists in the action of titanium tetrachloride on a mixture of alcohols in presence of pyridine and ammonia.

3. Members of a previously undescribed class of compounds have been prepared: triisopentyl isopropyl orthotitanate, ethyl isopentyl orthotitanate, allyl triisopentyl orthotitanate, triisopentyl propyl orthotitanate, isopentyl tripropyl orthotitanate, triallyl isopentyl orthotitanate, and diallyl diisopentyl orthotitanate.

When this paper was already prepared for publication, an article [8] appeared in which the preparation of some dialkyl diaryl orthotitanates by the partial transesterification of tetrabutyl orthotitanate is described. The products described, however, were not purified in any way, and the analytical results given for titanium are in good agreement also with an equimolecular mixture of the corresponding symmetrical alkyl orthotitanates. In the same paper the author refers to his preparation of 2-chloroethyl orthotitanate and benzyl orthotitanate, substances already described by us in 1951 [4].

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* See Consultants Bureau Translation, page 81

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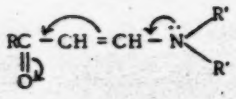
2-AMINOVINYL KETONES

COMMUNICATION 2. SOME REACTIONS OF ALKYL 2-DIALKYLAMINOVINYL KETONES

N. K. Kochetkov

In the previous communication [1], which was concerned with the synthesis of alkyl 2-dialkylaminovinyl ketones, we suggested, on the basis of an examination of the physical properties of these compounds, that their molecules possess high polarization:



Such polarization, of course, should be reflected in the chemical properties of alkyl 2-dialkylaminovinyl ketones, and some of these properties are examined in this paper.

In accord with the above scheme, which indicates an electronic displacement from the nitrogen to the carbonyl group, it may be expected that, in comparison with their saturated analogs, the Mannich bases, alkyl 2-dialkylaminovinyl ketones will show suppression of basic properties and reduced activity, both at the double bond and at the carbonyl group. The question of the reduction in basic properties has already been considered by us [1]. In order to decide the question of the activity of the double bond, we have studied the catalytic hydrogenation of these compounds.

The question of the hydrogenation of vinylogs of amides, to which class alkyl 2-dialkylaminovinyl ketones belong, cannot be regarded as settled. The results of one group of investigators [2] indicate that vinologs of amides (more complex in structure than the compounds that we have prepared) do not undergo normal hydrogenation, but suffer hydrogenolysis at the C – N bond. On the other hand, the results of other authors indicate that 1-dimethylamino-1,4-hexadien-3-one $CH_3CH = CHCOCH = CHN(CH_3)_2$ undergoes normal hydrogenation at both double bonds.

Our experiments on the hydrogenation of alkyl 2-dialkylaminovinyl ketones have shown that these compounds absorb hydrogen with great difficulty. Thus, when palladium on carriers (charcoal, barium carbonate) is used, hydrogenation stops completely when about 0.05 of a molecular proportion of hydrogen has been absorbed. When platinum oxide is used, hydrogenation again goes very slowly: in the course of 10-15 hours one molecule of hydrogen is absorbed, and in all cases about half of the original alkyl 2-dialkylaminovinyl ketone remains in the reaction mixture and, owing to hydrogenolysis of the C – N bond, a saturated ketone is formed. We have made a detailed investigation of the hydrogenation of 4-diethylamino-3-buten-2-one in presence of platinum. From the reaction mixture we isolated some of the original substance, and we showed that 2-butanone, identified as the dinitrophenylhydrazone, and diethylamine, isolated as the picrate, were formed. None of the normal reaction product (4-diethylamino-2-butanone) was formed. It may be concluded from this behavior that the primary reaction during hydrogenation leads to cleavage of the C – N bond, and the 3-buten-2-one formed is hydrogenated at the double bond:

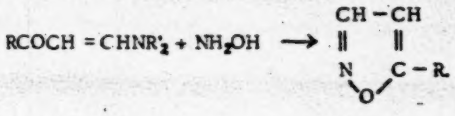
$$CH_3COCH = CHN(C_2H_5)_2 \xrightarrow[(Pt)]{H} NH(C_2H_5)_2 + CH_3COCH = CH_2 \longrightarrow CH_3COC_2H_5.$$

The other possibility – first hydrogenation of the double bond, and then hydrogenolysis – must be excluded, since it is well known that Mannich bases form amino alcohols when hydrogenated, and do not undergo hydrogenolysis at the C – N bond [4].

Our experiments, therefore, confirm the results concerning the hydrogenolysis of vinologs of amides and raise doubts concerning the results of British authors, which indicate that alkyl 2-aminovinyl ketones undergo normal hydrogenation [3]. Our results indicate not only the lability of the C – N bond, but also the strong suppression of the double bond in alkyl 2-dialkylaminovinyl ketones.

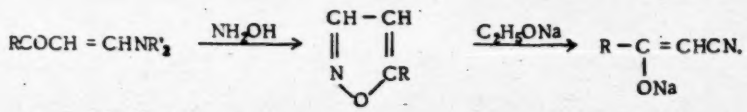
A second fact that demonstrates particularly clearly the deactivation of the double bond is the complete loss of dienophilic activity in aminovinyl ketones. As is well known, α,β-unsaturated ketones are among the most active dienophiles. 3-Buten-2-one, for example, reacts very vigorously with cyclopentadiene [5]. Alkyl 2-chlorovinyl ketones, though not reacting so vigorously, are still very active dienophiles [6, 7], and they condense to the extent of 70-85% with cyclopentadiene at room temperature. On the contrary, 4-dimethylamino-3-buten-2-one does not react with cyclopentadiene, one of the most active dienes, even when heated for many hours at 180°: it may all be recovered unchanged.

In order to clarify the question of the activity of the carbonyl group in alkyl 2-dialkylaminovinyl ketones, it was of interest to study their reaction with nitrogenous bases. It might be supposed [8] that, owing to the mobility of the dialkylamino group, the reaction would go in a way similar to that already found by us for alkyl 2-chlorovinyl ketones [9, 10], i.e., would be accompanied by cyclization and formation of the corresponding heterocycle. We selected the reaction of alkyl 2-dialkylaminovinyl ketones with hydroxylamine for detailed investigation. It was found that, when alkyl 2-dialkylaminovinyl ketones were heated with hydroxylamine in methanol for 5-6 hours, alkylisoxazoles were formed smoothly in 65-85% yield, so that in this respect dialkylaminovinyl ketones react like 2-chlorovinyl ketones. Investigation of the alkylisoxazoles formed, however, showed that there is an essential difference between these reactions. When alkyl 2-chlorovinyl ketones react with hydroxylamine hydrochloride, then as Kochetkov, Nesmeyanov, and Semenov showed [10], the isoxazoles obtained consist of a mixture of 3- and 5-alkyl compounds (γ - and α-isomers), in which there is 60% of 5-alkylisoxazole. Treatment of the alkylisoxazoles obtained from alkyl 2-dialkylaminovinyl ketones with sodium alkoxide, following Claisen [11], gave the sodium salt of the corresponding β-keto nitrile in more than 90% yield. This indicates that the isoxazoles formed consist mainly of 5-alkylisoxazole (α-isomer), and it is possible, considering the imperfections of the Claisen method from the analytical point of view, that pure α-isomer is actually obtained. The dominant direction of the reaction between aminovinyl ketones and hydroxylamine may therefore be expressed by the equation



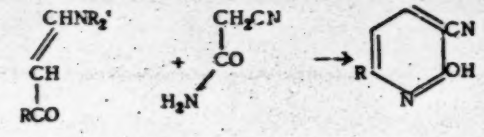
This result indicates quite definitely that the first step in the reaction is the replacement of the dialkylamino group by a hydroxylamine residue, after which cyclization occurs. It will be seen from this that the functions of the carbonyl group in 2-aminovinyl ketones, unlike those of the carbonyl group of 2-chlorovinyl ketones (which give about 40% of γ-isomer, formed by primary reaction of hydroxylamine at the carbonyl), are largely suppressed, so that it does not exhibit its typical reactivity toward a nucleophilic reagent, such as hydroxylamine. This is quite understandable from the point of view of the hypothesis advanced above concerning the great electronic displacement in the molecule of an aminovinyl ketone, leading to a reduction of the positive charge on the carbonyl carbon.

The condensation of alkyl 2-dialkylaminovinyl ketones with hydroxylamine is of importance also from the preparative point of view. By the aid of this reaction pure, or almost pure, 5-alkylisoxazoles can be prepared, and these have previously been difficultly accessible. The cleavage of 5-alkylisoxazoles by means of sodium alkoxide has an interest of its own, since by this means, from aminovinyl ketones via isoxazoles, very difficultly accessible β-keto nitriles can be obtained with an overall yield of 60-65%:



The possibilities for the utilization of 2-aminovinyl ketones for the synthesis of heterocyclic compounds are not confined to the preparation of isoxazoles. We have previously described the synthesis of 6-alkyl-2-hydroxynicotinonitriles by the condensation of acetals of β-keto aldehydes with 2-cyanoacetamide in presence of piperidine acetate [12]. We then suggested that this reaction goes through the intermediate formation of 2-(1-piperidyl)aminovinyl ketones. With the object of verifying this supposition, we have studied the reaction of alkyl

2-dialkylaminovinyl ketones with 2-cyanoacetamide, and we have found that this reaction proceeds very smoothly when a mixture of the reactants is heated in aqueous solution, the product being a 6-alkyl-2-hydroxynicotinonitrile:



This reaction is appreciably more rapid than the condensation of acetals of β-keto aldehydes with 2-cyanoacetamide, and, what is more important, it does not require the use of a condensing agent. This is a strong argument in favor of our views on the mechanism of the reaction of acetals of β-keto aldehydes with 2-cyanoacetamide [12], and we are inclined to the opinion that the condensations of 2-hydroxyvinyl ketones [14] and β-diketones [13] with 2-cyanoacetamide in presence of pyridine also go according to a similar scheme, i.e., via the intermediate formation of a 2-(1-piperidyl)aminovinyl ketone.

From the preparative point of view, the modified synthesis of substituted 2-hydroxypyridines described in this paper must be preferred to our previously developed synthesis via acetals of β-keto aldehydes, for reaction with 2-aminovinyl ketones is more rapid; also, the latter substances are more convenient to work with and can be prepared in better yields than acetals of β-keto aldehydes. The variant of the synthesis that we now propose is rendered simpler also by the fact that it is not necessary to isolate the 2-aminovinyl ketone from the reaction mixture: the aqueous solution obtained by the condensation of an alkyl 2-chlorovinyl ketone with a secondary amine, which contains the 2-aminovinyl ketone and a small excess of amine, is heated with 2-cyanoacetamide, and the hydroxynicotinonitrile separates rapidly in a yield that does not differ appreciably from that obtained when working by the original method [12]. In this form, the synthesis of 2-hydroxypyridines, which is essentially based directly on alkyl 2-chlorovinyl ketones, is the most convenient of the known methods for the synthesis of these compounds.

We have also investigated the reaction of alkyl 2-dialkylaminovinyl ketones with the Grignard reagent. 4-Dimethylamino- or 4-diethylamino-3-buten-2-one was treated with methylmagnesium iodide under the usual conditions, and after hydrolysis of the reaction mixture, 3-penten-2-one was isolated in about 20% yield and identified in the form of the dinitrophenylhydrazone:

$$CH_3COCH{=}CHN(CH_3)_2 + CH_3MgI \rightarrow CH_3COCH{=}CHCH_3.$$

This result is deserving of attention, particularly in view of the fact that simple alkyl 2-chlorovinyl ketones are known to react with organomagnesium compounds in the usual way, forming 2-chlorovinylcarbinols [15]. We again appear to have an example of the relative inactivity of the carbonyl group of a 2-dialkylaminovinyl ketone toward a nucleophilic reagent, in consequence of which the attack is directed to the β-carbon atom. The question of whether the reaction goes by 1,4-addition of the organomagnesium compound or by direct replacement of the dialkylamino group requires special investigation. We are inclined to the second supposition, because the formation of 3-penten-2-one can be established in the reaction mixture before it is hydrolyzed.

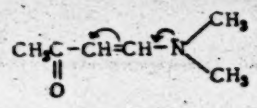
It was considered also that an investigation of the reaction of 2-dialkylaminovinyl ketones with alkyl halides would be of interest. In this case, owing to the conjugation of the electron pair of the nitrogen atom with the double bond, transfer of the reaction center could be expected; such transfer, according to Nesmeyanov's results [16], plays a decisive part in the reactions of systems of this sort. We have as yet investigated only one example of this reaction.

When 4-dimethylamino-3-buten-2-one was heated with excess of methyl iodide, a crystalline substance was quickly precipitated from the reaction mixture; it was readily soluble in water and contained halide ions; in analysis it corresponded to an addition product from one molecule of methyl iodide and one mole of the aminovinyl ketone. This compound was hydrolyzed with boiling water, and 4-hydroxy-3-methyl-3-buten-2-one $CH_3COC(CH_3){=}CHOH$ was isolated from the reaction mixture. The overall reaction may, therefore, be represented by the equation:

$$CH_3COCH{=}CHN(CH_3)_2 + CH_3I \xrightarrow{H_2O} CH_3COC(CH_3){=}CHOH + (CH_3)_2NH \cdot HI.$$

It is more convenient to carry out this reaction without isolating the intermediate addition product: 4-dimethylamino-3-buten-2-one is heated with an excess of methyl iodide, water is added to the reaction mixture, the excess of methyl iodide is driven off by heat, and the reaction product is extracted with ether. By this means the hydroxymethylbutenone was isolated in 17.4% yield.

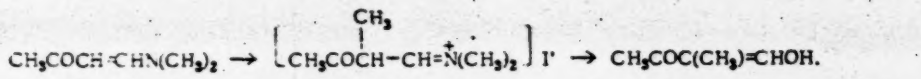
Reaction of methyl iodide with 4-dimethylamino-3-buten-2-one, therefore, proceeds with transfer of the reaction center, the nucleophilic attack being directed to the β-carbon atom:



It should be noted in this connection that dialkylaminoethyl ketones (the so-called Mannich bases) form normal alkiodides. In the saturated isologs of aminovinyl ketones, therefore, the transfer of reaction center no longer occurs. Why, in the alkylation of a dialkylaminovinyl ketone, the reaction center is not transferred to the end of the conjugated system (formation of an O-derivative) remains obscure.

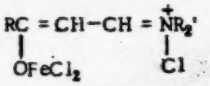
It is probable that, when methyl iodide reacts with 4-dimethylamino-3-buten-2-one, there is direct alkylation at the α-carbon atom, and not rearrangement of an initially formed methiodide. This view is supported by the fact that in the methylation of 4-diethylamino-3-buten-2-one, again only 4-hydroxy-3-methyl-3-buten-2-one is formed, and the 4-hydroxy-3-ethyl-3-buten-2-one $CH_3COC(C_2H_5)=CHOH$ that might be expected is not formed.

Our reaction can probably be represented by the following scheme:



We have found one reaction in the literature that is close in character to the one described. Robinson [17], investigating the reaction of ethyl 3-diethylaminocrotonate with methyl iodide, found that when the reaction mixture was hydrolyzed ethyl 2-methylacetoacetate was obtained. In a further study of this reaction, other authors [18], using ethyl iodide, also concluded that direct alkylation at carbon occurred.

Our investigation of the properties of alkyl 2-dialkylaminovinyl ketones has, therefore, indicated the highly peculiar nature of these compounds. It should be mentioned further that all of the compounds obtained give a color with ferric chloride. It is possible that this is to be explained by hydrolysis of the aminovinyl ketone to a β-keto aldehyde. It may be, however, that the nature of this phenomenon is more complex, for when anhydrous ferric chloride is added to a solution of an aminovinyl ketone in absolute ether, an intensely colored, ether-insoluble oil is precipitated. This indicates that the colored compound has a saltlike structure, for example



Such a hypothesis, though not yet confirmed experimentally, is in accord with the general character of alkyl 2-dialkylaminovinyl ketones.

EXPERIMENTAL

Hydrogenation of 4-Diethylamino-3-buten-2-one

4-Diethylamino-3-buten-2-one (5.0 g) was hydrogenated in alcohol (40 ml) in presence of platinum oxide (0.15 g) at room temperature. Absorption of hydrogen was very slow: 750 ml of hydrogen (calculated for one molecule 800 ml) was absorbed in 11 hours, and hydrogenation then came practically to a stop. The catalyst was filtered off, and the filtrate was distilled from a water bath, a fraction boiling up to 85° being collected. The residue was vacuum-distilled, and it all came over at 122-124° (5 mm) (2.1 g). After a second distillation the substance had b.p. 123-124° (5 mm) and n_D^{20} 1.5358, which corresponds to the constants of the original 4-diethylamino-3-buten-2-one.

The fraction of the filtrate boiling up to 85° at normal pressure was acidified with 10 ml of 10% hydrochloric acid and again distilled to dryness. The distillate was saturated with dinitrophenylhydrazine, and on the next day the crystals that had precipitated were filtered off and recrystallized from alcohol (orange-red needles, m.p. 114-115°). A mixture melting point with the dinitrophenylhydrazone of 2-butanone showed no depression.

The dry residue from the distillation was treated with 20% caustic soda and extracted with ether. The extract was washed with water, dried over magnesium sulfate, and saturated with picric acid. The precipitated crystals were filtered off and recrystallized from alcohol, yielding yellow crystals, m.p. 153-154°. A mixture melting point with diethylamine picrate showed no depression.

5-Methylisoxazole

A mixture of 14.0 g of 4-diethylamino-3-buten-2-one, 7.5 g of hydroxylamine hydrochloride, and 40 ml of methanol was heated for five hours. A hot solution of 70 g of cadmium chloride in 50 ml of water was then added to the hot reaction mixture, and after a few hours the crystals that had precipitated were filtered off, pressed dry on the filter, slightly moistened with water, and dry-distilled from a small distillation flask. The lower layer of the distillate was separated, and the upper layer was saturated with ammonium chloride and extracted with ether. The main portion of the product and the extract were united and then dried over magnesium sulfate. The ether was driven off, and the residue was distilled from a flask having a small fractionation column. The whole (4.9 g, 59%) came over at 121-122°. After redistillation the methylisoxazole had the following constants: b.p. 121-122° (750 mm); d_4^{20} 1.0224; n_D^{20} 1.4368; found MR 21.28; calculated for C_4H_5ONF MR 21.39 (nitrogen increment 2.84 [10]).

The substance (1.0686 g) was dissolved in alcohol (10 ml) and treated, under cooling, with an alcoholic solution of sodium ethoxide (1.0 g of sodium in 5 ml of alcohol), when a precipitate quickly formed. After 30 minutes 30 ml of absolute ether was added, and the precipitate was filtered off, washed with absolute ether, and dried in a vacuum. The weight of the sodium derivative of acetoacetonitrile was 1.244 g, corresponding to a content of 92% of the 5-methyl isomer. The phenylhydrazone of acetoacetonitrile was prepared by treating the sodium derivative with phenylhydrazine in aqueous medium, a little acetic acid being added. Recrystallization from alcohol yielded colorless crystals, m.p. 100-101°. The literature [19] gives m.p. 101-102° for the phenylhydrazone of acetoacetonitrile.

5-Propylisoxazole

A mixture of 13.0 g of 1-dimethylamino-1-hexen-3-one, 7.5 g of hydroxylamine hydrochloride, and 40 ml of methanol was heated for five hours, and to the mixture three times its volume of water was then added. The oil that separated was extracted with ether, the extract was dried with magnesium sulfate, the ether was driven off, and the residue was distilled from a flask having a small fractionation column. The fraction of b.p. 159-161° (9.0 g, 89%) was collected. After redistillation the propylisoxazole had the following constants: b.p. 161.0-161.5°; d_4^{20} 0.9682; n_D^{20} 1.4460; found MR 30.61; calculated for C_6H_9ONF MR 30.63; nitrogen increment 2.84 (cf. [10]).

Found %: N 12.54; 12.62

C_6H_9ON. Calculated %: N 12.60

The propylisoxazole was a colorless oil of characteristic odor.

The substance (1.0120 g) was treated with an alcoholic solution of sodium ethoxide (1 g of sodium in 15 ml of alcohol), as described for the previous experiment. The weight of precipitated sodium derivative of 3-oxohexanenitrile was 1.1214, which corresponds to a content of 91.4% of the 5-isomer. The phenylhydrazone of 3-oxohexanenitrile was prepared by the method given for the previous experiment; after crystallization from alcohol it melted at 96°.

Found %: N 21.03; 21.10

$C_{12}H_{15}N_3$. Calculated %: N 20.88

2-Hydroxy-6-methylnicotinonitrile

a) A mixture of 5.0 g of 4-dimethylamino-3-buten-2-one, 4.5 g of 2-cyanoacetamide, and 50 ml of water was heated at the boil, and after 10-15 minutes a crystalline precipitate of the condensation product began to form. After two hours at the boil, the mixture was cooled and the precipitate filtered off. The filtrate was boiled for a further two hours, and the small amount of precipitate that formed on cooling was filtered off and added to the main portion of the substance (4.1 g, 65%). Recrystallization from water yielded colorless needles, m.p. 278-280°. A mixture melting point with an authentic sample of 2-hydroxy-6-methylnicotinonitrile showed no depression. For this substance the literature gives m.p. 276-278° [12].

b) 4-Chloro-3-buten-2-one (5.0 g) was added slowly to 25 ml of a cooled, vigorously stirred 40% aqueous solution of dimethylamine. A solution of 5.0 g of 2-cyanoacetamide in 20 ml of water was then added, and the mixture was heated to the boil. After 15 minutes the condensation product began to crystallize out, and after one hour the mixture was cooled and the precipitate filtered off (3.9 g, 59%). Recrystallization from water yielded colorless needles, m.p. 279-281°.

2-Hydroxy-6-propylnicotinonitrile

A mixture of 2.1 g of 1-dimethylamino-1-hexen-3-one, 1.5 g of 2-cyanoacetamide, and 20 ml of water was heated at the boil for five hours. The mixture was cooled, and the crystalline precipitate was filtered off and washed

with cold water (1.75 g, 72%). Recrystallization from water yielded colorless needles, m.p. 147-148°. A mixture melting point with 2-hydroxy-6-propylnicotinonitrile showed no depression. For this substance the literature gives m.p. 147-148° [12], 153° [14].

2-Hydroxy-6-isobutylnicotinonitrile

This was prepared following a similar procedure from 3.5 g of 1-dimethylamino-5-methyl-1-hexen-3-one and 2.7 g of 2-cyanoacetamide. The condensation product came down as an oil, which then rapidly and completely crystallized. Recrystallization from alcohol yielded colorless needles, m.p. 148-149° (2.9 g, 74.8%). For 2-hydroxy--6-isobutylnicotinonitrile the literature [14] gives m.p. 149-150°.

Reaction of 4-Dimethylamino-3-buten-2-one with Methylmagnesium Iodide

A solution of 41.0 g of 4-dimethylamino-3-buten-2-one in an equal volume of ether was added slowly to a vigorously agitated, cooled (ice and salt) solution of methylmagnesium iodide prepared in the usual way from 47.0 g of methyl iodide and 7.0 g of magnesium in 250 ml of ether. An oil was precipitated, and this rapidly crystallized; the characteristic sharp odor of 3-penten-2-one appeared in the reaction mixture. The mixture was stirred for three hours at room temperature, and 10% hydrochloric acid was then added under cooling until the precipitate was completely dissolved. The ether layer was separated, and the aqueous layer was repeatedly extracted with ether. The extracts were dried over magnesium sulfate, and the ether was distilled off from a flask fitted with a good fractionating column. Distillation of the residue followed, a fraction boiling at 119-124° being collected. The redistilled substance had the following constants: b.p. 121-123°; d_4^{20} 0.8573; n_D^{20} 1.4390; found MR 25.81; calculated for C_5H_8O, MR 24.83. The yield was 6.9 g (19.8%). For 3-penten-2-one the literature [20] gives: b.p. 122-124°; d_4^{20} 0.8577; n_D^{20} 1.4390.

The dinitrophenylhydrazone was prepared in alcohol and recrystallized from the same solvent, yielding orange-red needles, m.p. 153-154°.

Found %: N 21.09; 21.32
$C_{11}H_{12}O_4N_4$. Calculated %: N 21.21

A mixture melting point with the dinitrophenylhydrazone of 3-penten-2-one showed no depression.

Reaction of 4-Dimethylamino-3-buten-2-one with Methyl Iodide

a) A mixture of 25.0 g of 4-dimethylamino-3-buten-2-one and 52.0 g of methyl iodide was heated at the boil for six hours. When the reaction mixture was cooled, an appreciable quantity of crystals separated. Water (50 ml) was added to the mixture, and it was again heated at the boil for 30 minutes, when the greater part of the methyl iodide was driven off with steam. The mixture was cooled and extracted with ether. The extracts were dried over sodium sulfate, the ether was driven off, and the residue was distilled. A fraction of b.p. 145-150° was collected; it solidified completely in the receiver. It was redistilled and then subjected to slow sublimation; the product (3.4 g, 17.5%) had b.p. 145-148°, m.p. 72°.

Found %: C 59.49; 59.53; H 8.18; 8.38
$C_5H_8O_2$. Calculated %: C 59.98; H 8.05

The substance, which was obtained as colorless, readily volatile crystals, was soluble in organic solvents and difficultly soluble in water. It gave a reddish-violet color with ferric chloride. For 4-hydroxy-3-methyl-3-buten--2-one the literature [21] gives b.p. 145-147°, m.p. 73°.

b) A mixture of 6.0 g of 4-dimethylamino-3-buten-2-one, 9.0 g of methyl iodide, and 30 ml of dry benzene was heated at the boil for four hours, and was then set aside for several days. The crystalline precipitate of condensation product was filtered off and recrystallized from absolute alcohol, yielding slightly colored crystals (4.5 g, 33%), m.p. 120-122° (dec.).

Found %: N 5.71; 5.62
$C_7H_{14}ONI$. Calculated %: N 5.48

The crystals were readily soluble in water, but did not dissolve in hydrocarbons. When silver nitrate was added to the aqueous solution, a precipitate of silver iodide quickly appeared. When the substance was treated with boiling water, as described above, 4-hydroxy-3-methyl-3-buten-2-one, identical with that obtained by direct hydrolysis of the reaction mixture, was isolated.

It is my pleasant duty to express my thanks to A. N. Nesmeyanov for his valuable advice and constant interest in the work.

SUMMARY

1. When alkyl 2-dialkylaminovinyl ketones are hydrogenated, hydrogenolysis of the nitrogen–carbon bond occurs, resulting in the formation of a saturated ketone and a secondary amine.

2. When alkyl 2-dialkylaminovinyl ketones react with hydroxylamine, 5-alkylisoxazoles are formed; this provides a convenient method for the synthesis of these compounds.

3. When alkyl 2-dialkylaminovinyl ketones react with 2-cyanoacetamide, 6-alkyl-2-hydroxynicotinonitriles are formed.

4. When 4-dimethylaminoamino-3-buten-2-one reacts with methylmagnesium iodide, 3-penten-2-one is formed.

5. The reaction of 4-dimethylamino-3-buten-2-one goes with transfer of reaction center, and, as a result, 4-hydroxy-3-methyl-3-buten-2-one is formed.

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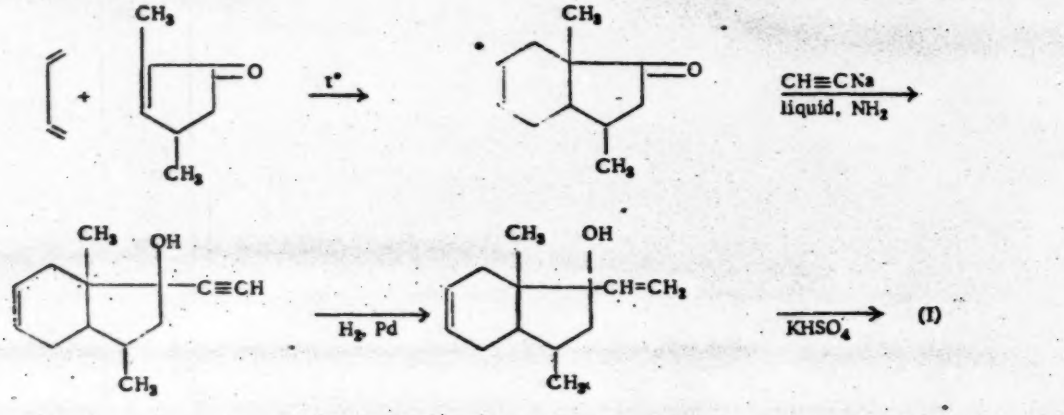
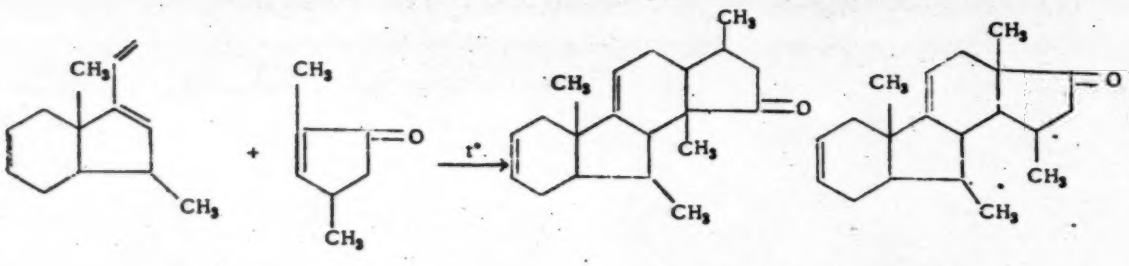
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XXIV. CONDENSATION OF 3a,4,7,7a-TETRAHYDRO-1,3a-DIMETHYL-3-VINYLINDENE WITH α,β-UNSATURATED CYCLIC KETONES

I. N. Nazarov and M. S. Burmistrova

In one of our previous communications [1] we described the synthesis of 3a,4,7,7a-tetrahydro-1-3a-dimethyl--3-vinylindene (I) and the diene condensation of this substance with 2,4-dimethyl-2-cyclopenten-1-one (II), which led to the preparation of the tetracyclic ketone III having a B-norcardosterane skeleton (Nazarov's nomenclature for synthetic steroids, see [2]):





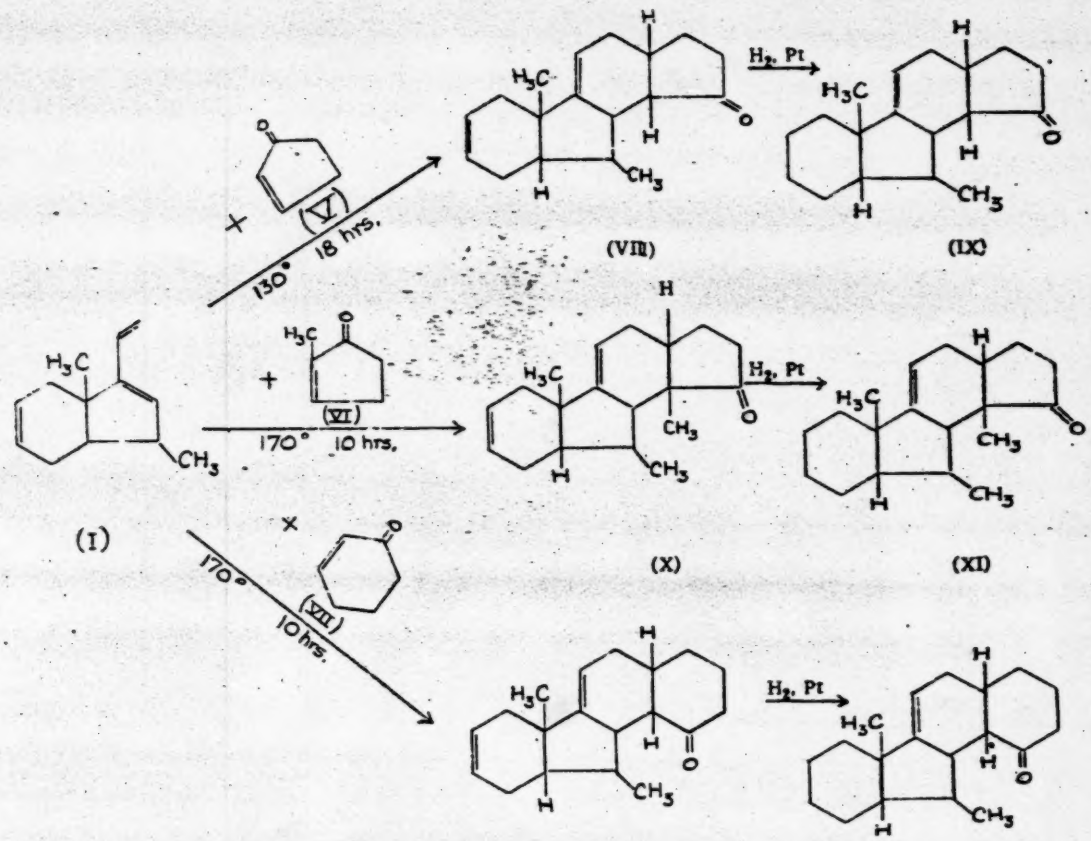
(I) (II) (III) (IV)

As we have shown in this laboratory in other cases [3], in diene condensations of α,β-unsaturated cyclic ketones with bicyclic dienes of the type 1-vinyl-Δ^1-octahydronaphthalene or 1-vinyl-Δ^1-hexahydroindene, the products always consist of mixtures of isomeric steroid ketones having the so-called "inverted" structure (having an inverted D-ring; Formula III), which differ among themselves either in spatial arrangement or in the position of the double bond formed in the diene condensation. Steroid ketones having the normal disposition of the D-ring (Formula IV) are apparently not formed in these condensations.

In the present investigation we have studied the diene condensations of 3a,4,7,7a-tetrahydro-1-3a-dimethyl-3-vinylindene (I) with 2-cyclopenten-1-one (V), 2-methyl-2-cyclopenten-1-one (VI), 2-cyclohexen-1-one (VII),

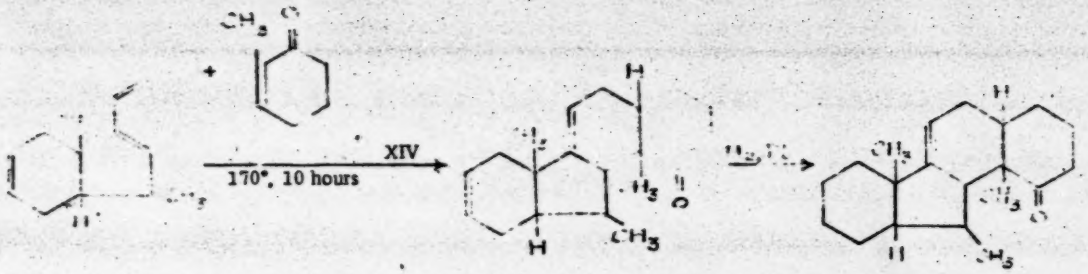
2-methyl-2-cyclohexen-1-one (XIV), and also with citraconic anhydride (XVII) and p-benzoquinone (XX). These condensations were carried out by heating the diene I at 130-170° with excess of the ketone in presence of a carbon dioxide atmosphere or of 1% of dimethylaniline in a sealed glass tube.

As a result of the condensation of the diene I with the cyclopentenone V, the methylcyclopentenone VI, and the cyclohexenone VII, yields of 30-40% were obtained of mixtures of isomers of 7,10-dimethyl-2,9-B-norcardosteradien--15-one (VIII), 7,10,14-trimethyl-2,9-B-norcardosteradien-15-one (X), and 7,10-dimethyl-2,9-B-norcardochrysadien--15-one (XII) respectively, in the form of viscous oils that did not crystallize even when strongly cooled (−35°, two hours):



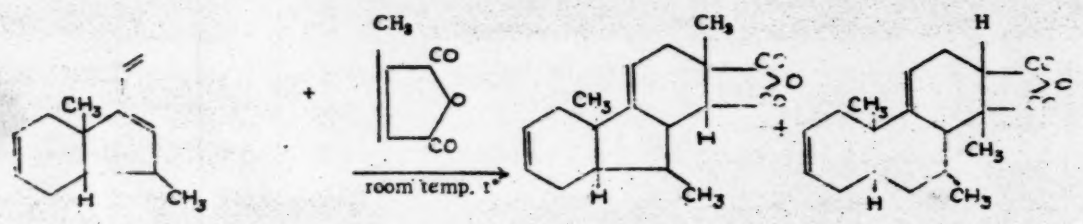
When the 2,9-diene steroid ketones VIII, X, and XII were hydrogenated in presence of a platinum catalyst, only one molecule of hydrogen was absorbed, and the corresponding Δ^9-steroid ketones IX, XI, and XIII were formed; these also were viscous noncrystallizing oils. As we have shown in other cases [3], when 2,9-diene steroid ketones are hydrogenated, only one double bond (position 2, ring A) is reduced, the double bond in the 9-position not being affected; usually, this bond is hydrogenated only with great difficulty (high temperature and pressure).

When the diene I was condensed with 2-methyl-2-cyclohexen-1-one (XIV), a viscous oil was again obtained, but this partially crystallized after long standing. Both the liquid and the crystalline solid corresponded in composition to the expected product of this diene condensation, i.e., 7,10,14-trimethyl-2,9-B-norcardochrysadien-15-one (XV). When this ketone was hydrogenated in presence of a platinum catalyst, one molecule of hydrogen was absorbed and 7,10,14-trimethyl-9-B-norcardochrysanen-15-one (XVI) was formed:



(I) (XV) (XVI)

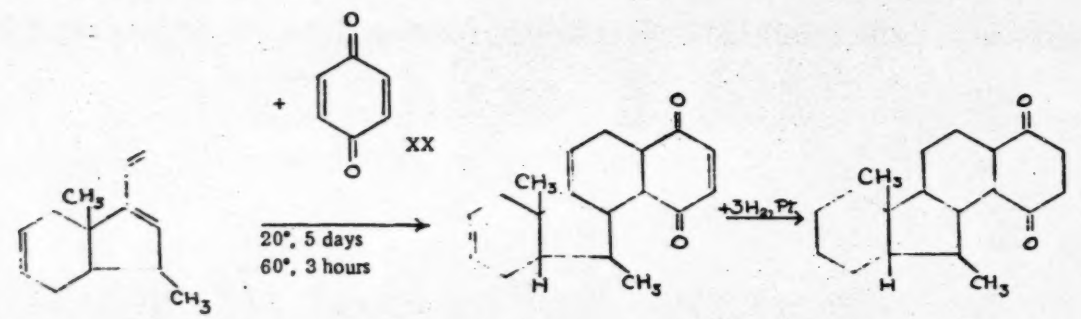
The condensation of the diene I with citraconic anhydride (XVII) was carried out at room temperature in benzene solution or by boiling with glacial acetic acid. In this condensation a very viscous oil was obtained, which did not crystallize when cooled to −35°; this, by analogy with other similar condensation reactions studied in our laboratory, should be a mixture of two isomeric anhydrides (XVIII and XIX):



(I) (XVII) (XVIII) (XIX)

A mixture of the corresponding acids was obtained in the form of a noncrystallizing oil by hydrolysis of the condensation product with alkali or aqueous acetic acid.

The condensation of the diene I with p-benzoquinone (XX) was effected by heating a mixture of the components in dioxane solution in a sealed glass tube at 60°. The condensation product formed pale-yellow crystals, m.p. 166° and consisted of 7,10-dimethyl-2,9.16-D-norcardochrysatriene-15,17a-dione (XXI). When this diketone was hydrogenated in presence of a platinum catalyst, three molecules of hydrogen were absorbed and the corresponding tetracyclic diketone (XXII) was formed; it formed colorless crystals, m.p. 141°.



(I) (XXI) (XXII)

In conclusion it must be pointed out that none of the tetracyclic ketones described in this paper give characteristic crystalline derivatives with semicarbazide, and, with the exception of the diketone XXI, which gives a normal

derivative, they all form products with 2,4-dinitrophenylhydrazine that have extended melting-point ranges and give a high nitrogen content in the analysis.

EXPERIMENTAL

1-Ethynyl-3a,4,7,8a-tetrahydro-3,7a-dimethyl-1-indanol

A solution of 9.2 g of sodium in 350 ml of liquid ammonia was placed in a three-necked flask fitted with mechanical stirrer and thermometer, and it was then stirred vigorously and cooled with dry ice (−70°) while a current of dry acetylene was passed at 20 liters per hour for three hours. Stirring of the sodium acetylide was continued and acetylene was passed (at 10 liters per hour) while a solution of 33 g of 3a,4,7,8a-tetrahydro-3-7a-dimethyl--1-indanone (b.p. 92-92.5° at 7 mm; n_D^{25} 1.4912) [1] in 75 ml of absolute ether was added at −70° over a period of 30 minutes, after which stirring and passage of acetylene was continued for one hour. The reaction mixture was left overnight in a bath of dry ice. On the next day practically the whole of the ammonia was removed, and additions were made of 100 ml of ether, 35 g of ammonium chloride, and 150 ml of water (from a dropping funnel). The ether layer was separated, and the aqueous layer was carefully extracted with ether. The product was washed with water, dried with sodium sulfate, and fractionated, yielding 33.4 g (87.4%) of 1-ethynyl-3a,4,7,8a-tetrahydro--3,7a-dimethyl-1-indanol, b.p. 88-90° at 3 mm; n_D^{24} 1.5070 [1].

The partial hydrogenation of this acetylenic alcohol in presence of a Pd catalyst (one molecule of hydrogen) yielded the previously described [1] 3a,4,7,8a-tetrahydro-3,7a-dimethyl-1-vinyl-1-indanol.

3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene (I)

A mixture of 3 g of 3a,4,7,8a-tetrahydro-3,7a-dimethyl-1-vinyl-1-indanol (b.p. 88-90° at 3.5 mm; n_D^{20} 1.5045) and 1.5 g of freshly calcined, finely ground potassium hydrogen sulfate was heated at 120° for ten minutes under reduced pressure (95 mm). When cool, the mixture was carefully extracted with ether, the potassium hydrogen sulfate was filtered off, and the ethereal solution was washed with water, dried with calcium chloride, and fractionally distilled, yielding 2.2 g of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinylindene (I), b.p. 60-62° at 1.5 mm; n_D^{25} 1.5070 [1].

Condensation of 3a,4,7,7a-Tetrahydro-1-3a-dimethyl-3-vinylindene with 2-Cyclopenten -1-one

A mixture of 5 g of the diene I and 10 g of 2-cyclopenten -1-one (V) (b.p. 43-45° at 17 mm; n_D^{20} 1.4605) [4] was heated at 130° for 18 hours in a sealed glass tube filled with carbon dioxide. The mixture was then vacuum-fractionated, yielding 3 g of a mixture of tetracyclic ketones (VIII) in the form of a viscous yellow oil that did not crystallize when cooled to −35°; b.p. 132-134° (0.034 mm); n_D^{20} 1.5400; d_4^{20} 1.048; calculated MR 75.60; found MR 76.67.

Found %: C 84.30; 84.47; H 9.31, 9.37
$C_{18}H_{24}O$. Calculated %: C 84.31; H 9.45

Hydrogenation of the Tetracyclic Ketones VIII

A solution of 2 g of the above-described mixture of isomeric tetracyclic ketones (VIII) in 20 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. The saturation of two double bonds would have required the absorption of 345 ml of hydrogen, and in the course of four hours 210 ml of hydrogen was actually absorbed. The hydrogenation product was vacuum-fractionated, yielding 1.5 g of a mixture of isomers of 7,10--dimethyl-9-B-norcardosteren-15-one (IX) in the form of a colorless viscous oil, b.p. 123-126° (0.03 mm); n_D^{20} 1.5288; d_4^{20} 1.043; calculated MR 76.07; found MR 76.33.

Found %: C 83.08; 83.14; H 10.45; 10.40
$C_{18}H_{26}O$. Calculated %: C 83.45; H 10.15

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with 2-Methyl-2-cyclopenten -1-one

A mixture of 4 g of the diene I and 4.8 g of 2-methyl-2-cyclopenten -1-one (XI) (b.p. 53-55° at 15 mm; n_D^{20} 1.4756) [4] was heated at 170° for ten hours in a sealed glass tube filled with carbon dioxide. The mixture was then vacuum-fractionated, yielding 1.5 g of a mixture of the isomeric tetracyclic ketones X in the form of a viscous yellow oil that did not crystallize when cooled to −35°; it had b.p. 133-138° (0.03 mm); n_D^{20} 1.5380; d_4^{20} 1.037; calculated MR 80.29; found MR 81.40.

Found %: C 85.85; 85.75; H 10.01; 9.95
$C_{19}H_{26}O$. Calculated %: C 84.40; H 9.70

Hydrogenation of the Tetracyclic Ketones X

A solution of 1.3 g of the above-described mixture of isomeric tetracyclic ketones (X) in 15 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 225 ml of hydrogen was required for the saturation of two double bonds, and actually 225 ml of hydrogen was absorbed in 20 minutes. The hydrogenation product was vacuum-fractionated and yielded 1 g of a mixture of isomers of 7,10,14-trimethyl-9-B-norcardosteren--15-one (XI) in the form of a very viscous colorless liquid, b.p. 140-142° (0.04 mm); n_D^{29} 1.5280; d_4^{29} 1.019; calculated MR 80.70; found MR 82.25.

Found %: C 84.49; 84.52; H 10.80; 10.68
$C_{19}H_{28}O$. Calculated %: C 83.76; H 10.40

Condensation of 3a,4,7,7a-Tetrahydro-1-3a-dimethyl-3-vinylindene with 2-Cyclohexen-1-one

A mixture of 5 g of the diene I and 50 g of the 2-cyclohexen-1-one (VII) (b.p. 67° at 19 mm; n_D^{20} 1.4850) [4] was heated at 170° for ten hours in a sealed glass tube filled with carbon dioxide. The mixture was then vacuum-fractionated, and yielded 3 g of the isomeric tetracyclic ketones XII in the form of a yellow viscous oil, which did not crystallize when cooled to −35°; it had b.p. 150.5-151° (at 0.07 mm); n_D^{20} 1.5375; d_4^{20} 1.0533; calculated MR 80.22; found MR 80.12.

Found %: C 84.10; 83.96; H 9.96; 10.13
$C_{19}H_{28}O$. Calculated %: C 84.40 H 9.70

Hydrogenation of the Tetracyclic Ketones XII

A solution of 1.5 g of the above-described mixture of isomeric tetracyclic ketones (XII) in 15 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 248 ml of hydrogen was required for the saturation of two double bonds, and the actual volume of hydrogen absorbed in one hour was 200 ml. The hydrogenation product was vacuum-fractionated, and yielded 1.2 g of a mixture of isomers of 7,10-dimethyl-9-B-norcardochrysanen-15-one (XIII) in the form of a colorless viscous oil, b.p. 132-134.5° (0.035 mm); n_D^{28} 1.5215; d_4^{20} 1.0433; calculated MR 80.70; found MR 79.51.

Found %: C 83.13; 82.92; H 10.75; 10.56
$C_{19}H_{28}O$. Calculated %: C 83.76; H 10.40

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with 2-Methyl-2-cyclohexen-1-one

A mixture of 4 g of the diene I and 45 g of 2-methyl-2-cyclohexen-1-one (XIV) (b.p. 64-64.5° at 15 mm; n_D^{20} 1.4802) [4] was heated at 170° for ten hours in presence of 0.5 g of dimethylaniline in a sealed glass tube. The mixture was then vacuum-fractionated, and yielded 2.5 g of a mixture of the isomeric tetracyclic ketones XV in the form of a viscous yellow oil, b.p. 147-150° (0.032 mm); n_D^{28} 1.5415; d_4^{20} 1.056; Calculated MR 84.84; Found MR 84.60.

Found %: C 85.05, 85.06; H 10.03, 9.89
$C_{20}H_{28}O$. Calculated %: C 84.45; H 9.92

After long standing, the oil obtained partially crystallized out: 0.25 g of colorless crystals, m.p. 139-142° (from ether) was obtained.

Found %: C 84.46, 84.21; H 9.93, 9.84
$C_{20}H_{28}O$. Calculated %: C 84.45; H 9.92

Hydrogenation of the Tetracyclic Ketones XV

A solution of 1.3 g of the above-described mixture of isomeric tetracyclic ketones (XV) in 10 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 205 ml of hydrogen was required for the saturation of two double bonds, and the actual volume of hydrogen absorbed in 15 hours was 107 ml. The hydrogenation product was vacuum-fractionated, and yielded 1.2 g of a mixture of isomers of 7,10,14-trimethyl-9-B-norcardochrysanen-15-one (XVI) in the form of a colorless viscous oil, b.p. 148-150° (0.07 mm); n_D^{26} 1.5288; d_4^{20} 1.033; Calculated MR 85.23; Found MR 85.43.

Found %: C 83.72, 83.88; H 10.70, 10.62
$C_{20}H_{30}O$. Calculated %: C 83.86; H 10.50

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with Citraconic Anhydride

A mixture of 5.1 g of the diene I, 3.8 g of citraconic anhydride (XVII) (n_D^{20} 1.4712), and 1 ml of dry benzene was set aside for five days at room temperature. The residue after removal of benzene was vacuum-fractionated, and yielded 3.5 g of a mixture of isomeric anhydrides (XVIII and XIX) in the form of a very viscous yellow oil, which did not crystallize when cooled to − 35° and then rubbed out with various organic solvents; it had b.p. 144-145° (0.012 mm); n_D^{20} 1.5310; d_4^{20} 1.137; Calculated MR 77.25; Found MR 77.88.

	Found %:	C 75.87, 75.66; H 7.80, 7.86
$C_{15}H_{22}O_3$.	Calculated %:	C 75.50; H 7.75

Hydrolysis of this product with alcoholic alkali or 50% acetic acid resulted in the formation of a noncrystallizing mixture of acids.

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with p-Benzoquinone

A solution of 2 g of the diene I and 1 g of p-benzoquinone (m.p. 116°) in 20 ml of dioxane was sealed in a glass tube filled with carbon dioxide, left at room temperature for one day, and then heated at 60° for three hours. The residue that remained after removal of dioxane under somewhat reduced pressure (100-110 mm) partially crystallized, and 1.8 g of yellowish crystals of the tetracyclic diketone XXI, m.p. 155-159° was filtered off. After two recrystallizations from methanol the product melted at 166-166.5°.

	Found %:	C 80.93, 80.69; H 8.30, 8.02
$C_{15}H_{22}O_2$.	Calculated %:	C 80.79; H 7.86

The 2,4-dinitrophenylhydrazone melted at 213-215°.

	Found %:	N 11.64, 12.26
$C_{28}H_{26}O_5N_4$.	Calculated %:	N 12.12

Hydrogenation of the Adduct

A solution of 0.75 g of crystals of m.p. 166-166.5° in 10 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 180 ml of hydrogen was required for the saturation of three double bonds, and in 15 minutes 190 ml of hydrogen was actually absorbed. The dioxane was removed under reduced pressure (110 mm), and the residue crystallized. Filtration yielded 0.7 g of crystals of 7,10-dimethyl-B-norcardochrysane-15,-17a-dione (XXII), m.p. 132-135.5°, which after two recrystallizations from ether melted at 140.5-141°.

	Found %:	C 78.92, 78.95; H 9.49, 9.61
$C_{19}H_{28}O_2$.	Calculated %:	C 79.11; H 9.80

SUMMARY

1. 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene (I) has been caused to undergo the diene condensation with 2-cyclopenten-1-one (V), 2-methyl-2-cyclopenten-1-one (VI), 2-cyclohexen-1-one (VII), 2-methyl-2-cyclohexen-1-one (XIV), p-benzoquinone, and citraconic anhydride.

2. In this way 30-40% yields have been obtained of the corresponding tetracyclic steroid ketones VIII, X, XII, XV, and XXI, which have B-norcardosterane and B-norcardochrysane skeletons.

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Institute of Organic Chemistry
of the USSR Academy of Sciences

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[3] I. N. Nazarov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 901, 920, 929 (1953). ***

[4] I. N. Nazarov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 889 (1953).****

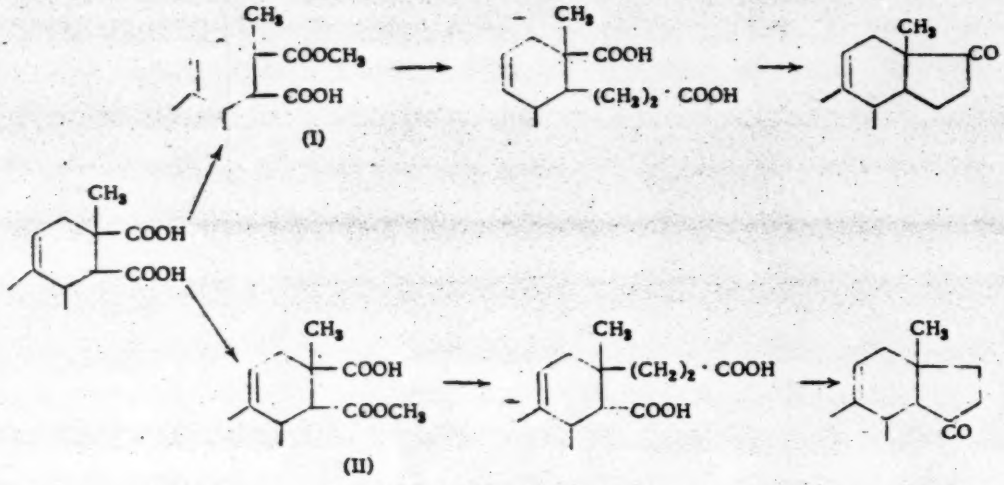
* See Consultants Bureau Translation, page 911
** See Consultants Bureau Translation, page 651
*** See Consultants Bureau Translation, page 799, 817, 827
**** See Consultants Bureau Translation, page 787

SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS

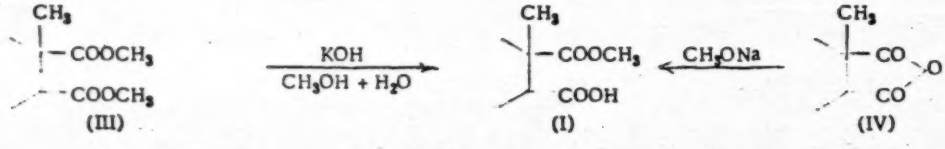
COMMUNICATION XXII. STEREOCHEMISTRY OF POLYCYCLIC COMPOUNDS. II. MONOESTERS OF THE CIS AND TRANS FORMS OF 1-METHYL-1,2-CYCLOHEXANEDICARBOXYLIC AND 1-METHYL-4-CYCLOHEXENE-1,2-DICARBOXYLIC ACIDS, AND THEIR REACTIONS•

I. N. Nazarov and V. F. Kucherov

For the synthesis of polycyclic compounds related to steroids from cyclic 1,2-dicarboxylic acids by lengthening of a carbon chain followed by cyclization, it is necessary to have the corresponding monoesters of types (I) and (II).



Having developed an accessible method for the synthesis of anhydrides and diesters of cis and trans forms of 1-methyl-1,2-cyclohexanedicarboxylic acid and 1-methyl-4-cyclohexene-1,2-dicarboxylic acid [1], we have made a detailed study, for these model cases, of various methods for the preparation of monoesters of types (I) and (II). Monoesters of type (I), applicable to the synthesis of steroid compounds, can be prepared either by the partial hydrolysis of diesters (III) with one equivalent of alkali in aqueous methanol [2], or by the action of sodium alkoxide on an alcoholic solution of the anhydride (IV) [3, 4]



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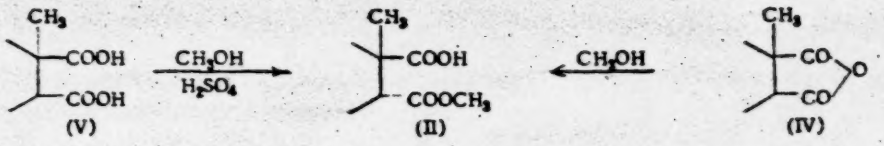
By these methods it is generally possible to prepare monoesters in which the carboxyl group on the tertiary carbon atom is esterified.

On the other hand, by the action of alcohol on anhydrides (IV) [5], or by partial esterification of the corresponding dicarboxylic acids (V), monoesters of type (II) are preferentially formed; these have a free carboxyl group on the tertiary carbon atom

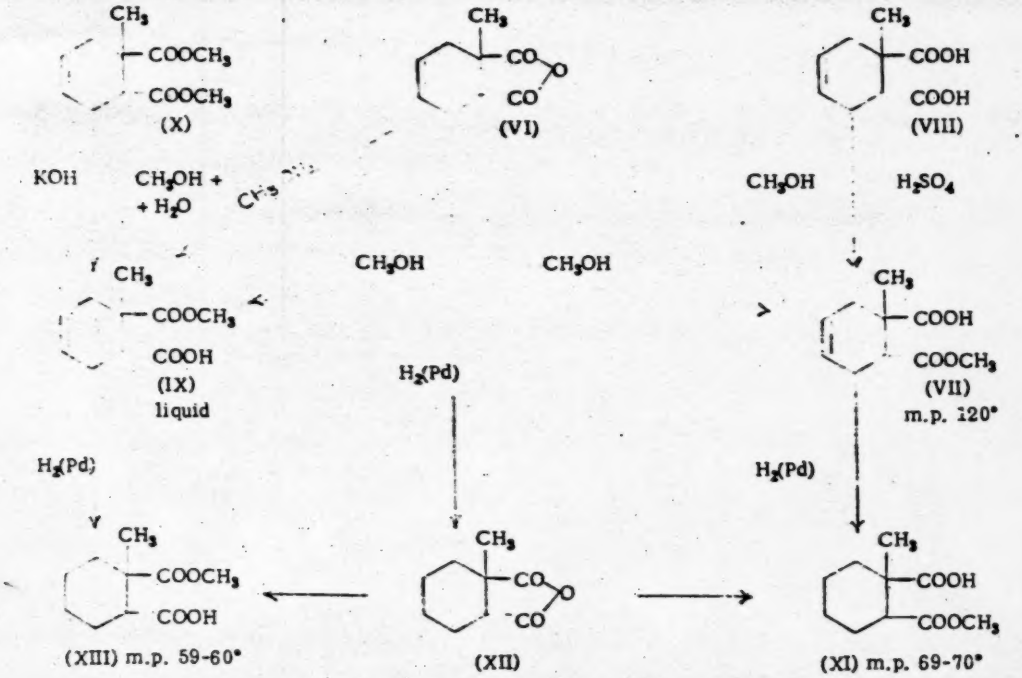


We have made a detailed study of all of these methods for the very simple model examples of cis- and trans-1-methyl-1,2-cyclohexanedicarboxylic and -1-methyl-4-cyclohexene-1,2-dicarboxylic acids, and we have obtained the following results.

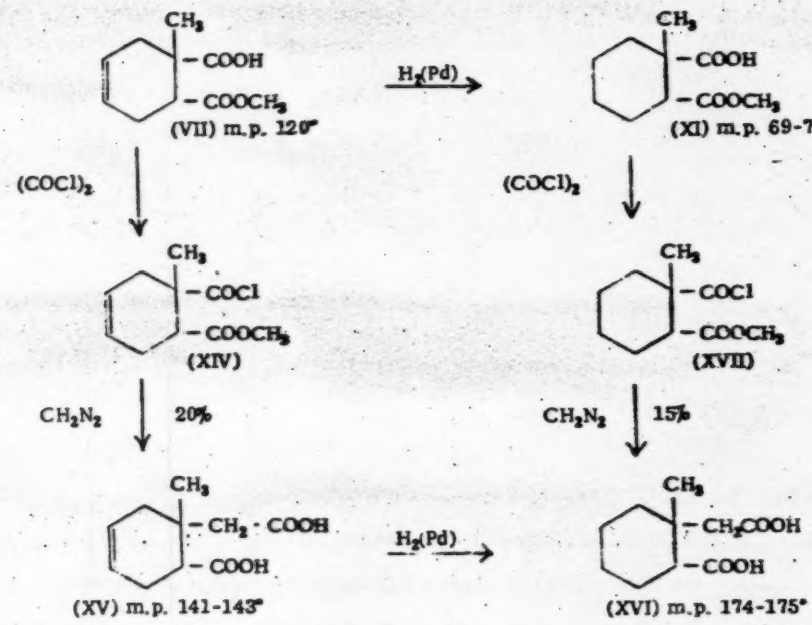
When the anhydride of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VI) was boiled with absolute methanol, a mixture of isomeric monoesters (VII and IX) of the cis series was obtained, the former predominating. By treatment of this mixture with petroleum ether and freezing out, a yield of about 45% of the pure crystalline secondary cis-monoester VII, m.p. 120-121°, was obtained. The same monoester in satisfactory yield was obtained also by the partial esterification of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VIII).

The isomeric liquid tertiary cis-monoester (IX) was obtained as main product when the cis-anhydride (VI) was heated with a solution of sodium methoxide in methanol, and also by the partial hydrolysis of the diester (X) with a solution of caustic potash in aqueous methanol. It did not appear to be possible to isolate this liquid cis-monoester (IX) in a completely pure form, for when it was vacuum-distilled, it lost methanol and was converted into the original anhydride (VI).

Hydrogenation of the crystalline cis-monoester (VII) in presence of a Pd catalyst yielded the crystalline saturated cis-monoester (XI), m.p. 69-70°, which was formed also when absolute methanol reacted with the saturated cis-anhydride (XII). When sodium methoxide reacted with the cis-anhydride (XII), the main reaction product was the isomeric tertiary cis-monoester (XIII), m.p. 59-60°, which was obtained also by the hydrogenation of the liquid monoester (IX) in presence of a Pd catalyst.



In order to prove the structures of the cis-monoesters obtained, they were converted into the corresponding acetic acid derivatives by Arndt-Eistert lengthening of the carbon chain. With oxalyl chloride, the monoester (VII) gave the acid chloride (XIV) in quantitative yield, and this, when treated with excess of diazomethane, was converted into a diester, which was hydrolyzed to the cis-acid (XV). Owing to steric hindrance, this reaction did not go smoothly, and the acid (XV) was obtained in low yield (about 20%). Hydrogenation of the acid (XV) in presence of a Pd catalyst yielded the known cis-2-carboxy-1-methylcyclohexaneacetic acid (XVI), m.p. 174-175° [6]. A low yield (about 15%) of the same acid was obtained also from the unsaturated monoester (XI) via the acid chloride (XVII) by the Arndt-Eistert reaction:

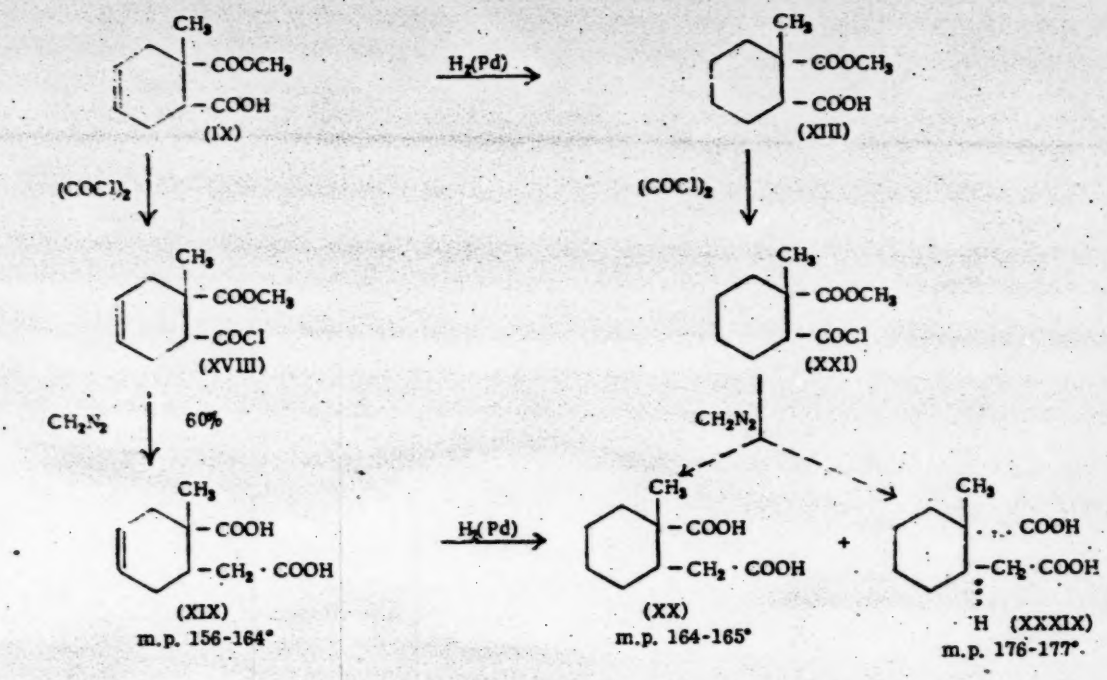


The course of the Arndt-Eistert reaction with the tertiary cis-monoesters (IX) and (XIII) is very interesting. It was found that conversion of the acid chloride (XVIII) obtained from the liquid cis-monoester (IX) into the diazoketone, followed by rearrangement of this to a diester and hydrolysis of the diester with 20% caustic potash, finally gave a yield of about 60% of the crystalline cis-acid (XIX), m.p. 156-164°, which was found to be considerably contaminated with the trans isomer (XXXVIII). Fractional crystallization of this mixture did not lead to the separation of individual substances. However, after hydrogenation of the mixture in presence of a Pd catalyst, fractional crystallization from acetone and aqueous acetone yielded both a pure cis-acid (XX), m.p. 164-165° and a trans isomer (XXXIX), m.p. 176-177°, which was prepared also from the trans-monoester (XXIX) by the Arndt-Eistert reaction (see below). Both of these acids have been described previously [2, 7]. This unexpected stereoisomerization in the Arndt-Eistert reaction was confirmed by us in the case of the pure saturated crystalline cis-monoester (XIII).

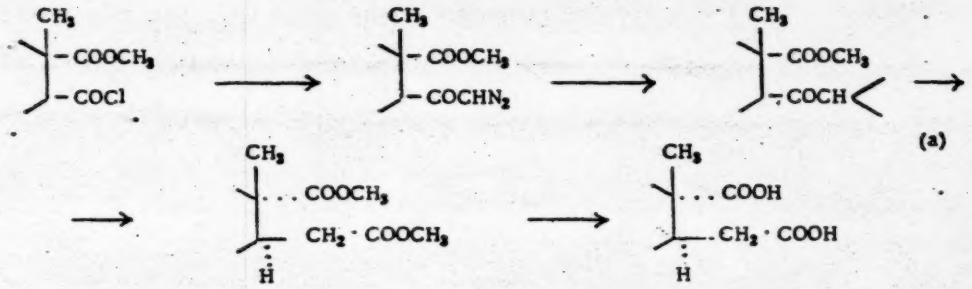
When the Arndt-Eistert reaction was carried out on the cis-acid chloride (XXI) obtained from the cis-monoester, a crystalline mixture of approximately equal amounts of the cis-acid (XX), m.p. 164-165°, and the trans-acid (XXXIX), m.p. 176-177°, was obtained, and these substances were isolated in the pure form by fractional crystallization. There can be no doubt that the original acid chloride (XXI) belongs to the cis series: it was quantitatively hydrolyzed into pure cis-1-methyl-1,2-cyclohexanedicarboxylic acid.

The above-described stereoisomerization occurs, therefore, in the course of the Arndt-Eistert reaction, most probably at the stage at which decomposition of the diazo ketone occurs, a process that is known to occur by a free radical mechanism (see a, page 54).

Stereoisomerization in the course of an Arndt-Eistert reaction, which we have observed for the first time, may be associated with steric hindrance, which may exist when there is a cis-ortho-substituent having comparatively large bulk. We have shown that such steric effects occur in the formation of anilides. It was found that the



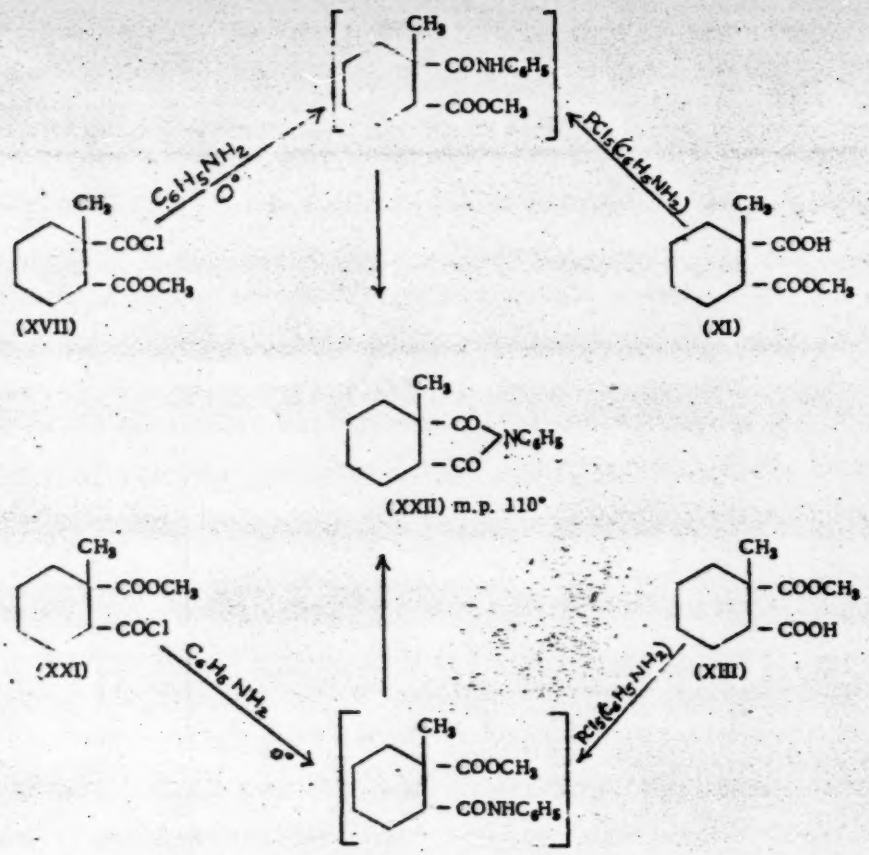
isomeric cis-acid chlorides (XVII) and (XXI), when treated in ether solution with excess of aniline at 15-20°, gave quantitative yields of the same crystalline amide (XXII) (m.p. 110°). The same product was obtained directly from the monoesters (XI) and (XIII) by the action of phosphorus pentachloride and aniline in the usual way [6]. In the



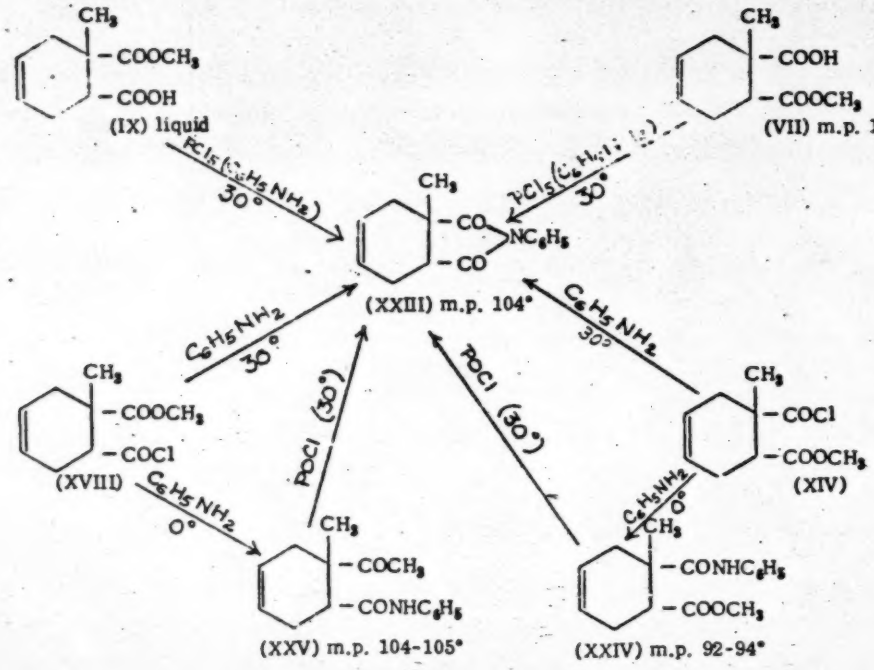
reaction of aniline with the acid chlorides (XVII) and (XXI), even under very mild conditions (0°), it was not found possible to isolate the corresponding anilides, which are apparently unable to exist, being spontaneously and completely converted into the imide (XXII) owing to the spatial proximity of the cis-ortho-methoxycarbonyl and anilide groups (see a, page 55).

The analogous reactions were investigated also for the cis-monoesters (VII) and (IX), which contain a double bond in the cyclohexane ring.

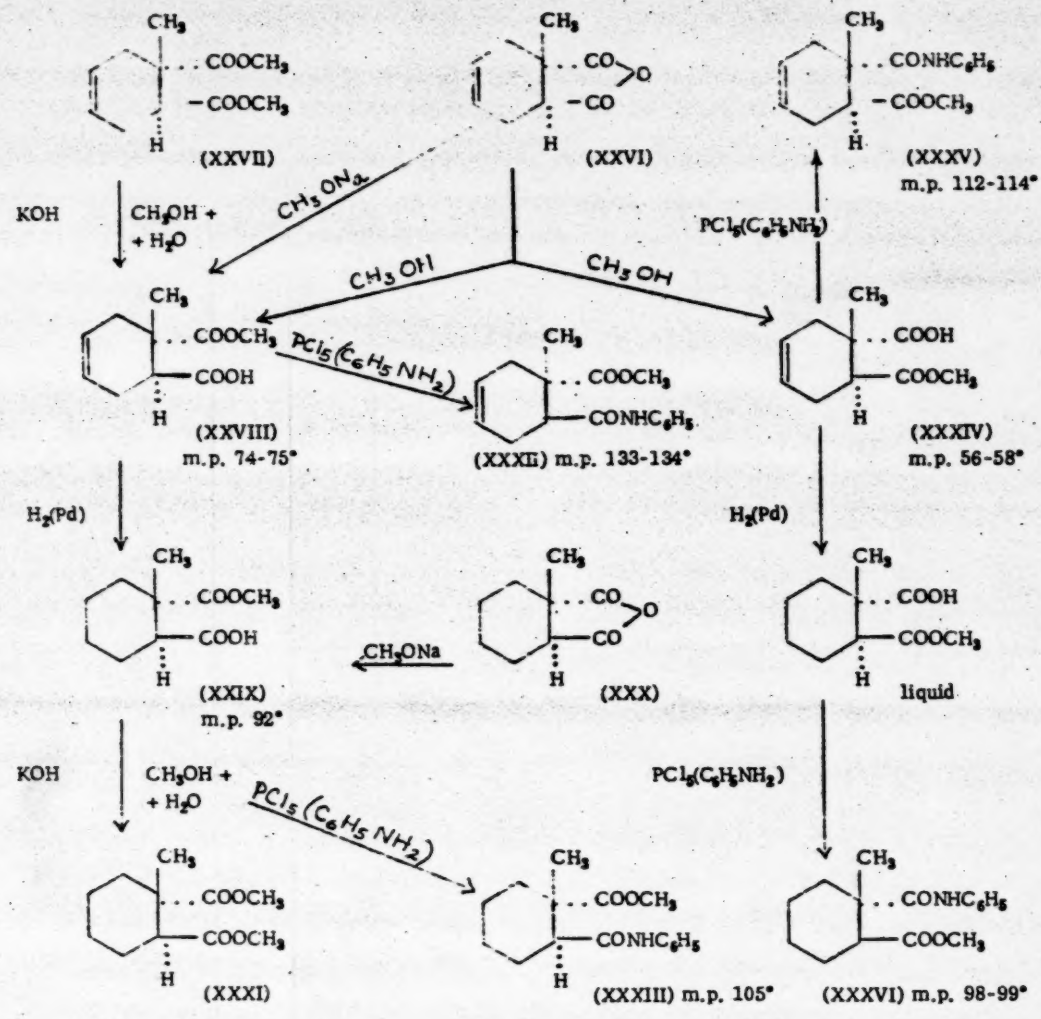
Both the monoesters (VII) and (IX) themselves, and also their acid chlorides (XIV and XVIII), give the same crystalline imide (XXIII), m.p. 103-104°, when treated with aniline at 20-30°. When, however, the acid chlorides (XIV) and (XVIII) reacted with aniline in ether solution at 0°, the corresponding crystalline anilides (XXIV and XXV) were isolated. They were quantitatively converted into the above-described crystalline imide (XXIII) when warmed in ether solution and with a small amount of phosphoryl chloride. This fact, which indicates the exceptionally high instability of the cis-anilides (XXIV) and (XXV), may be explained only by the spatial proximity of the methoxycarbonyl and anilide groups in the cis-ortho-positions. This is particularly evident from the examination of models, and it is confirmed by the fact of the ready formation of the imide of 1,2-cyclohexanedicarboxylic acid when the monoamide of this acid is heated [8].



Quite different behavior is observed for the monoesters of the trans series, the preparation and properties of which we have also studied in detail. When the trans-anhydride (XXVI) was treated with a methanolic solution of sodium methoxide, or when the trans-dimethyl ester (XXVII) was partially hydrolyzed, a 60-70% yield of the



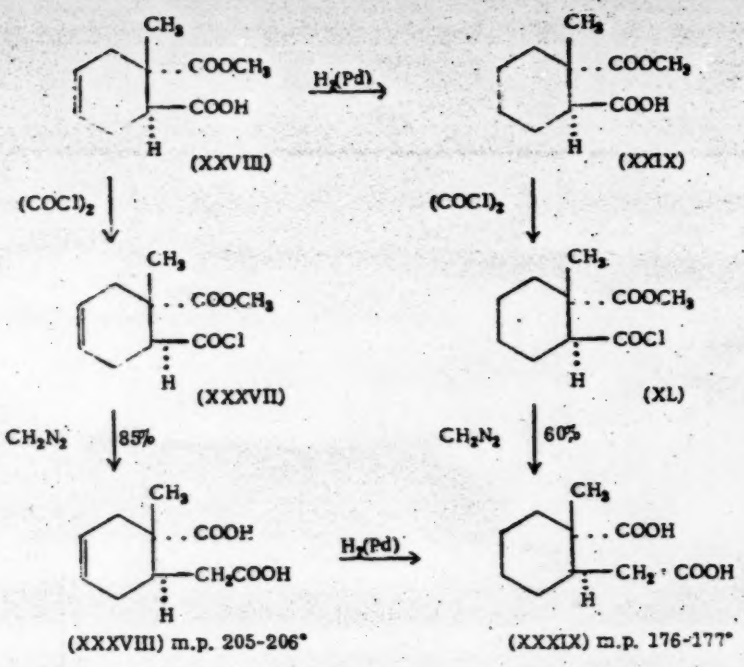
crystalline trans-monoester (XXVIII) m.p. 74-75°, was obtained, and hydrogenation of this in presence of a Pd catalyst yielded the known saturated monoester (XXIX) [2]. By the same methods this last substance can also be obtained in good yields from the saturated trans-anhydride (XXX) or by the partial hydrolysis of the corresponding trans-ester (XXXI). The trans-monoesters (XXVIII) and (XXIX) react with phosphorus pentachloride and aniline to give the crystalline trans-anilides (XXXII) and (XXXIII), which are fairly stable and are not converted, like the cis-anilides, into the corresponding imides.



When the trans-anhydride (XXVI) was boiled with absolute methanol, a mixture of the trans-monoesters (XXVIII) and (XXXIV) was obtained, the second monoester predominating. Owing to their similar solubilities and close melting points, the components of this mixture were difficult to separate, and the monoester (XXXIV) being difficultly accessible, was not studied in detail. The trans-monoester XXXIV gives a normal trans-anilide (XXXV); after being hydrogenated, it gives the new trans-anilide XXXVI. Both these anilides are quite stable and are not converted into amides.

For final confirmation of their structures, the trans-monoesters (XXVIII) and (XXIX) were converted by the Arndt-Eistert reaction into the corresponding acetic acid derivatives (see a, page 57).

Treatment of the acid chloride (XXXVII) with diazomethane, followed by conversion to the diester and hydrolysis, yielded the crystalline trans-acid (XXXVIII) in 85% yield, and this, after hydrogenation in presence of a Pd catalyst, gave the known trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX) [2]. The same trans-acid (XXXIX) was obtained in 60% yield from the pure trans-acid chloride (XL) by the Arndt-Eistert method. When the trans-acid chlorides (XXXVII) and (XL) were treated with excess of aniline in ether solution, quantitative



yields of the corresponding trans-anilides (XXXII) and (XXXIII) were obtained, and these were quite stable, which is in accord with their spatial configurations.

EXPERIMENTAL

carboxy^2-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (VII). a) A solution of 25 g of the cis-anhydride (VI) [b.p. 113-115° (4 mm); n_D^{25} 1.4890] [1] in 75 ml of absolute methanol was boiled under reflux for six hours. The methanol was distilled off under reduced pressure, and there remained a viscous liquid, which partially crystallized when treated with petroleum ether. The crystalline product was filtered off and washed with petroleum ether, yielding 12.2 g of a substance of m.p. 115-118°. From the liquid residue, after dissolution in petroleum ether with addition of a little diethyl ether followed by strong cooling, a further 1.3 g of crystalline substance, m.p. 113-115°, was isolated. The overall yield was 46.5%. Recrystallization from a mixture of benzene and petroleum ether (1:5) yielded the carboxy^2-monomethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VII), m.p. 120-121°.

	Found %:	C 60.77, 60.89; H 7.04, 6.98
$C_{10}H_{14}O_4$.	Calculated %:	C 60.65; H 7.12

The liquid reaction product (16.1 g) could not be caused to crystallize by standing and by treating with solvents; it had n_D^{20} 1.4875. When attempts were made to distil it under reduced pressure, it was almost completely converted into the original cis-anhydride (VI), and when hydrolyzed with alcoholic alkali it gave a quantitative yield of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VIII).

b) The cis-acid (VIII) (4 g; m.p. 167-168°) was dissolved in 100 ml of absolute methanol, 2.6 ml of concentrated sulfuric acid was added, and the solution was boiled in a water bath for two hours. Methanol was distilled off under reduced pressure until the volume fell to 25 ml, 30 ml of water was added, the reaction product was extracted with ether, and the ether solution was washed with water. The ether was distilled off, and the liquid esterification product that then remained partially crystallized when treated with petroleum ether. The crystalline product was filtered off and washed with petroleum ether (2.4 g, m.p. 105-110°). The product, after crystallization from a mixture of petroleum ether and benzene (5:1), melted at 119-120° and showed no depression in admixture with the above-described cis-monoester (VII) prepared from the cis-anhydride (VI) by the action of methanol. Vacuum distillation of the liquid residue yielded 1.2 g of the dimethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid, b.p. 104-106° (4 mm); n_D^{25} 1.4725.

carboxy^2-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (IX). a) The cis-anhydride (XI) (5 g) was added to a solution of 1.35 g of sodium in 40 ml of absolute methanol, and the mixture was boiled for one hour. After removal of methanol under reduced pressure, the solid residue of salts was dissolved in 20 ml of water, and the solution was mixed with charcoal, filtered, and then acidified to Congo red with hydrochloric acid. The reaction product was extracted with ether, and the ether solution was washed with water and dried with sodium sulfate. After removal of ether, 5.2 g of the carboxy^1-monomethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (IX) was obtained as a clear viscous liquid; n_D^{20} 1.4870.

	Found %:	C 61.00, 60.81; H 6.93, 6.93
$C_{10}H_{14}O_4$.	Calculated %:	C 60.65; H 7.12

b) To a solution of 0.55 g of caustic potash in 10 ml of water and 30 ml of methanol, 2 g of the dimethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (X) [b.p. 98° (2 mm); n_D^{20} 1.4746] was added, and the mixture was boiled under reflux for three hours. The methanol was distilled off under reduced pressure, and an aqueous solution of an ether extract of the residue was treated with charcoal and acidified with hydrochloric acid. The oil that separated, treated with petroleum ether and chilled, gave 0.03 g of a crystalline substance, which was found to be the above-described cis-monoester of m.p. 120° (VII). The liquid reaction product, after extraction with ether and removal of ether under reduced pressure, yielded 1.8 g of the carboxy^1-monomethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (IX) in the form of a clear viscous liquid; n_D^{20} 1.4870.

carboxy^2-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XI). a) A solution of 5.5 g of the cis-monoester (VII) in 35 ml of dry dioxane was hydrogenated in presence of a Pd catalyst. One molecule of hydrogen was absorbed (625 ml at 760 mm and 0°). The solvent was distilled off under reduced pressure, and the liquid hydrogenation product completely crystallized when treated with petroleum ether (5.1 g, m.p. 67-69°). Crystallization of petroleum ether yielded the carboxy^2-monomethyl ester of cis-1-methyl-1,2-cyclohexanedicarboxylic acid (XI), which had a constant melting point, 69-70°.

	Found %:	C 60.22, 59.94; H 8.32, 8.11
$C_{10}H_{16}O_4$.	Calculated %:	C 60.0; H 8.05

b) A solution of 3 g of the cis-anhydride (XII) in 20 ml of absolute methanol was boiled for five hours. The methanol was distilled off under reduced pressure, and the liquid mixture of monoesters was dissolved in petroleum ether and set aside to crystallize after being seeded with some pure monoester (XI). The product, 0.8 g of the crystalline monoester (XI), m.p. 65-68°, melted at 69-70° after recrystallization from petroleum ether and showed no depression in melting point when mixed with the previous sample.

carboxy^1-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XIII). a) The cis-anhydride (XII) (3.5 g) was added to a warm solution of 1 g of sodium in 25 ml of absolute methanol, and the solution was boiled in a water bath for three hours. The methanol was distilled off under reduced pressure, and the residue of salts was dissolved in 10 ml of water and acidified with hydrochloric acid. The viscous semicrystalline product that separated was extracted with ether, and the extract was dried with sodium sulfate. The ether was driven off, and the residue was dissolved in a small amount of petroleum ether by application of heat, and was set aside to crystallize while cooling. The product was 2.35 g of crystals, m.p. 57-58°. From the mother liquor, after removal of part of the solvent followed by strong cooling, a further 0.55 g of crystals was isolated (m.p. 56-58°). The overall yield was 69%. After being recrystallized from petroleum ether, the carboxy^1-monomethyl ester of cis-1-methyl-1,2-cyclohexanedicarboxylic acid (XIII) melted at 59-60°.

	Found %:	C 60.03, 60.06; H 8.12, 8.09
$C_{10}H_{16}O_4$.	Calculated %:	C 60.0; H 8.05

b) A solution of 3 g of the liquid monoester (IX) in 20 ml of dioxane was treated with hydrogen in presence of a Pd catalyst, and 340 ml of hydrogen (760 mm, 0°) was absorbed. The solvent was distilled off under reduced pressure, and the viscous liquid hydrogenation product was dissolved in a small amount of petroleum ether, from which, on cooling, 2.1 g of the crystalline cis-monoester (XIII), m.p. 58-59° and identical with the previous sample, was isolated.

Preparation of Acid Chlorides of cis-Monoesters

1. Acid Chloride of the carboxy^2-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XIV). Oxalyl chloride (10 ml) was added to a solution of 10 g of the cis-monoester (VII) in 100 ml of absolute benzene, and the mixtwe was set aside for one hour at room temperature. It was then heated for 30 minutes at 40-45°, and the benzene and excess of oxalyl chloride were distilled off. The liquid reaction product was vacuum-

distilled, and yielded 10.6 g of the cis-acid chloride (XIV), b.p. 99-99.5° (1 mm); n_D^{22} 1.4905.

Found %: Cl 16.41, 16.43
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.35

2. Acid Chloride of the carboxy[2]-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XVII). This was prepared by the same procedure from 5.7 g of the cis-monoester (XI) and 6 ml of oxalyl chloride in 60 ml of absolute benzene, and, after distillation, 5.7 g of the acid chloride (XVII) was obtained in the form of a colorless liquid, b.p. 110.5-111° (3.5 mm); n_D^{20} 1.4780.

Found %: Cl 16.21, 16.18
$C_{10}H_{15}O_3Cl$. Calculated %: Cl 16.17

3. Acid Chloride of the carboxy[1]-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-carboxylic Acid (XVIII). From 13 g of the liquid cis-monoester (IX) the usual procedure yielded 13.3 g of the acid chloride XVIII, b.p. 96-97° (1.5 mm); n_D^{22} 1.4865.

Found %: Cl 16.52, 16.65
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.35

4. Acid Chloride of the carboxy[1]-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XXI). From 3.8 g of the cis-monoester (XIII) and 5 ml of oxalyl chloride, the usual procedure yielded 3.7 g of the pure acid chloride (XXI), b.p. 112-112.5° (4 mm); n_D^{22} 1.4760.

Found %: Cl 16.19, 16.26
$C_{10}H_{15}O_3Cl$. Calculated %: Cl 16.17

cis-6-Carboxy-1-methyl-3-cyclohexene-1-acetic Acid (XV). A solution of 2 g of the cis-acid chloride (XIV) in 10 ml of absolute ether was added slowly with cooling to a dry ethereal solution of 2.1 g of diazomethane, and the mixture was set aside at room temperature for 24 hours. The ether was distilled off under reduced pressure, and the liquid residue of diazo ketone was dissolved with cooling in 45 ml of absolute methanol. Freshly prepared silver oxide (0.5 g) was added, and the mixture was boiled under reflux for six hours. The silver oxide was filtered off and washed with methanol. Methanol was distilled off under reduced pressure, and the liquid residue was hydrolyzed by treatment at the boil with 7 ml of 40% caustic potash and 5 ml of methanol for four hours. The methanol was distilled off, and the aqueous alkaline solution was treated with charcoal, filtered, and acidified with hydrochloric acid. The liquid reaction product separated and was extracted with ether. The ether extract was washed with water and dried, and the ether was driven off. The residue was dissolved in a small amount of acetone and the solution obtained was diluted with an equal volume of petroleum ether and allowed to stand, when a crystalline substance slowly separated. It was filtered off and washed with a mixture of acetone and petroleum ether (1:3). The product was 0.35 g of cis-6-carboxy-1-methyl-3-cyclohexene-1-acetic acid (XV), m.p. 136-140°. After recrystallization from a mixture of acetone and petroleum ether, the acid melted at 141-143°.

Found %: C 60.94, 60.80; H 7.11, 7.28
$C_{10}H_{14}O_4$. Calculated %: C 60.6; H 7.12

cis-2-Carboxy-1-methylcyclohexaneacetic Acid (XVI). a) A solution of 2.1 g of the cis-acid chloride (XVII) in 20 ml of absolute ether was added slowly with cooling to a dry ethereal solution of 2.1 g of diazomethane, and the mixture was set aside for 15 hours at room temperature. The ether was distilled off under reduced pressure, and the viscous residue was dissolved in 40 ml of absolute methanol. Silver oxide (0.5 g) was then added to the mixture, which was boiled for eight hours. The mixture was filtered, the methanol was distilled off under reduced pressure, and the residue was boiled with 10 ml of 40% caustic potash and 7 ml of methanol. The warm solution was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, and the residue was acidified with hydrochloric acid. The oil that separated was extracted with ether, the extract was washed with water, and the ether was distilled off. The residue was dissolved in a small amount of acetone, and an equal volume of petroleum ether was added. A crystalline product (0.28 g) came down after a time, and this, after recrystallization from a mixture of acetone and petroleum ether, melted at 174-175°. The literature [5] gives 172-173° for the melting point of cis-2-carboxy-1-methylcyclohexaneacetic acid.

Found %: C 59.87, 59.95; H 8.04, 8.10
$C_{10}H_{16}O_4$. Calculated %: C 60.0; H 8.05

b) A solution of 0.1 g of cis-6-carboxy-1-methyl-3-cyclohexane-1-acetic acid (XV) in absolute methanol was treated with hydrogen in presence of a Pd catalyst. The methanol was distilled off, and from the crystalline

product, after recrystallization from a mixture of acetone and petroleum ether, an acid was obtained that melted at 174-175° and showed no melting-point depression in admixture with the cis-acid (XVI) described above.

Reaction of the cis-Acid Chloride (XVIII) with Diazomethane. A solution of 5 g of the cis-acid chloride (XVIII) in 20 ml of absolute ether was added slowly to a dry ethereal solution of diazomethane prepared from 25 g of methylnitrosourea, and the mixture was set aside at room temperature for 24 hours. The ether was distilled off under reduced pressure, the residue was dissolved in 100 ml of methanol with cooling, 1 g of freshly prepared silver oxide was added, and the mixture was boiled for six hours. In the early stages of heating vigorous evolution of nitrogen was observed. A further 0.3 g of silver oxide was added, and boiling was continued for a further two hours. The mixture was treated with charcoal and filtered, the methanol was removed under reduced pressure, and the liquid residue was hydrolyzed by boiling it with 25 ml of 40% caustic potash and 20 ml of methanol for six hours. The dark-colored solution was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, and the residue was acidified with hydrochloric acid. A yellow partially solid reaction product was precipitated, and this practically completely solidified when cold. The crystalline product was filtered off and washed free from yellow resin with 50% aqueous acetone. The product was 2.6 g of acid, m.p. 157-163°, and from the aqueous solution and washings a further 0.2 g of the acid, m.p. 155-163°, was separated, the total yield being 60%. After repeated crystallizations from acetone, aqueous acetone, or a mixture of acetone and petroleum ether, crystals were obtained having an indefinite melting point (162-166°) and corresponding in analysis to 6-carboxy-6-methyl-3-cyclohexene-1-acetic acid (XIX).

	Found %:	C 60.86, 60.89; H 7.35, 7.32
$C_{10}H_{14}O_4$.	Calculated %:	C 60.6; H 7.12

The acid obtained (XIX, 1 g), m.p. 162-166°, was hydrogenated in 15 ml of absolute methanol in presence of a Pd catalyst. After removal of solvent, a clear viscous liquid was obtained, and this crystallized out when treated with petroleum ether and had m.p. 130-145°. The hydrogenation product was recrystallized from a mixture of acetone and petroleum ether (1:1), and 0.3 g of substance melting at 157-161° was obtained. After a further recrystallization it melted at 164-165°, the melting point of known cis-2-carboxy-2-methylcyclohexaneacetic acid (XX).

	Found %:	C 59.95, 60.0; H 8.19, 8.02
$C_{10}H_{16}O_4$.	Calculated %:	C 60.0; H 8.05

From the mother liquor, after two crystallizations from acetone, a small amount of a crystalline substance of m.p. 175-177° was isolated; it showed no melting-point depression in admixture with trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX) (see below).

Reaction of the cis-Acid Chloride (XXI) with Diazomethane. A solution of 3.0 g of the cis-acid chloride (XXI) in 20 ml of absolute ether was added slowly under cooling to a dry ethereal solution of 2.5 g of diazomethane, and the resulting mixture was set aside at room temperature overnight. The ether was distilled off under reduced pressure, the residue was dissolved, with cooling, in 60 ml of absolute methanol, 0.8 g of silver oxide was added, and the mixture was boiled in a water bath for eight hours. Vigorous evolution of nitrogen began at 40°. The mixture was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, and the liquid reaction product was boiled with 17 ml of 40% caustic potash and 17 ml of methanol for four hours. The dark-colored solution was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, the alkaline solution was acidified with hydrochloric acid, and the mixture was extracted with ether. The residue remaining after removal of ether was dissolved in a small amount of acetone, from which it slowly crystallized out, yielding 0.4 g of crystals, m.p. 168-173°, which after recrystallization from acetone melted at 175-177° and showed no depression in admixture with trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX). From the acetone mother liquor, after addition of an equal volume of petroleum ether, 0.5 g of a nonhomogeneous crystalline product, m.p. 125-140° was obtained. Two recrystallizations from a mixture of acetone and petroleum ether (1:1) yielded 0.2 g of pure cis-2-carboxy-2-methylcyclohexaneacetic acid (XX), m.p. 164-165°.

Anilides of cis-Monoesters, and their Reactions

1. Anilide of the carboxy^2-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXIV). A solution of 0.5 g of aniline in 5 ml of absolute ether was added slowly to a cooled (to − 5°) and stirred solution of 0.5 g of the cis-acid chloride (XIV) in 5 ml of absolute ether. The mixture was allowed to stand for 30 minutes at 0°. Water was then added, and the ether layer was separated, washed successively with 5% hydrochloric acid, 10% sodium carbonate, and water, and then dried. After removal of ether, an oily substance remained, and this solidified when treated with petroleum ether (0.60 g, m.p. 82-87°). After recrystallization from a mixture of diethyl

ether and petroleum ether, the anilide melted at 91-93°.

Found %: C 70.57, 70.58; H 6.96, 7.14; N 5.29, 5.11
$C_{16}H_{15}O_3N$. Calculated %: C 70.30; H 7.00; N 5.30

2. Anilide of the carboxy[1]-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXV). The procedure of the preceding experiment applied to 0.5 g of the cis-acid chloride (XVIII) and 0.5 g of aniline in ether yielded 0.50 g of a crystalline product, which melted after crystallization from a mixture of diethyl ether and petroleum ether at 104-105° and which corresponded in analysis to the cis-anilide (XXV).

Found %: C 70.54, 70.50; H 7.34, 7.10; N 5.12, 5.35
$C_{16}H_{15}O_3N$. Calculated %: C 70.30; H 7.00; N 5.30

3. Phenylimide of 1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXIII). a) Finely ground phosphorus pentachloride (0.6 g) was added to a solution of 0.4 g of the monoester (VII) (m.p. 120-121°) in 10 ml of absolute ether, and the mixture was heated until solution was complete. The solution was stirred at 20-25°, and 4 g of aniline was slowly added. The mixture was boiled for 30 minutes. Water was added, and the separated ether layer was carefully washed, successively with 10% hydrochloric acid, 5% sodium carbonate, and water. The ether was distilled off, and the yellow crystalline residue was washed on the filter with a mixture of diethyl ether and petroleum ether (1:1) (0.35 g of white crystals, m.p. 98-100°). In order to purify the product, it was dissolved in ether, and the ether solution, after filtration to remove undissolved impurities, was evaporated to low bulk, when an equal volume of petroleum ether was added. Needles of m.p. 103-104° separated, and they corresponded in composition to the phenylimide (XXIII).

Found %: C 74.47, 74.29; H 6.20, 6.42; N 5.94, 6.02
$C_{15}H_{13}O_2N$. Calculated %: C 74.66; H 6.26; N 5.80

b) In a similar way, 0.3 g of the liquid cis-monoester (IX) yielded 0.2 g of a crystalline substance, which melted after crystallization from ether at 103-104° and showed no melting-point depression in admixture with the imide (XXIII).

c) A solution of 0.5 g of aniline in 5 ml of ether was added to a stirred solution of 0.5 g of the cis-acid chloride (XIV) in 5 ml of absolute ether. The ether solution was boiled for 30 minutes, and then washed successively with 5% hydrochloric acid, 10% sodium carbonate, and water. The ether was distilled off, and the residue (0.6 g) was recrystallized from a small amount of ether, yielding 0.35 g of the imide (XXIII), m.p. 102-103°.

d) The same imide (XXIII) of m.p. 103-104° was obtained by the same method from the cis-acid chloride (XVIII).

e) A solution of 0.1 g of the cis-anilide (XXIV), m.p. 92-93°, in 4 ml of absolute ether and 0.2 ml of phosphoryl chloride were boiled together for one hour. The ether solution was washed successively with 10% sodium carbonate and water, and then dried. The ether was distilled off, and the residue, after crystallization from a mixture of diethyl ether and petroleum ether (1:1), melted at 102-103° and showed no melting-point depression in admixture with the imide (XXIII).

f) The same procedure applied to the anilide (XXV) yielded a crystalline product of m.p. 102-103°, identical with the imide (XXIII).

4. Phenylimide of 1-Methyl-1,2-cyclohexanedicarboxylic Acid (XXII). Phosphorus pentachloride (1.5 g) was added to an ethereal solution of 1 g of the cis-monoester (XI) (m.p. 69-70°), and the mixture was boiled until solution was practically complete. Aniline (10 ml) was added at 20-25°. The reaction mixture was treated with water, and the separated ether layer was washed successively with 10% hydrochloric acid, 10% sodium carbonate, and water, and then dried with sodium sulfate. The crystalline substance remaining after removal of ether was washed with a mixture of diethyl ether and petroleum ether (1:4), and yielded 0.95 g of a substance of m.p. 105-107°. Crystallization from diethyl ether containing a little petroleum ether gave a pure product, m.p. 109-110°, which corresponded in analysis to the phenylimide (XXII).

Found %: C 74.21, 74.35; H 7.02, 6.89; N 5.65, 5.67
$C_{15}H_{17}O_2N$. Calculated %: C 74.05; H 7.04; N 5.75

The same product was prepared in an analogous way from the isomeric-cis monoester (XIII); it had the same melting point (110-111°). From each of the isomeric acid chlorides (XVII) and (XXI), both with cooling (0°) and with warming (30-35°), the same imide of m.p. 109-110° was obtained by reaction with aniline, and this imide was identical with the above-described phenylimide (XXII).

carboxy[1]-Monomethyl Ester of trans-1-Methyl-4-cyclohexene-1,2-carboxylic Acid (XXVIII). a) The anhydride of trans-1-methyl-4-cyclohexene-1,2-carboxylic acid (XXVI, 3.5 g) was added slowly to a warm solution of 1 g of sodium in 30 ml of absolute methanol and boiled for one hour. The methanol was distilled off under reduced pressure, and the residue was dissolved in 20 ml of water. The solution was treated with charcoal, filtered, and acidified with hydrochloric acid to Congo red. A liquid reaction product separated, and this solidified almost completely after standing. The solid was filtered off, and washed with water and with a mixture of diethyl ether and petroleum ether (1:5) (2.2 g of crystals, m.p. 71-74°). The liquid part, after long standing, yielded a further 0.25 g of crystals, m.p. 70-73°; the total yield was 60%. After crystallization from petroleum ether the trans-monoester (XXVIII) had a constant melting point of 74-75°.

Found %: C 60.64, 60.57; H 7.29, 7.05
$C_{10}H_{14}O_4$. Calculated %: C 60.60; H 7.12

Anilide: Finely ground phosphorus pentachloride (0.75 g) was added to a solution of 0.5 g of the trans-monoester (XXVIII) in 20 ml of absolute ether. The mixture was heated until solution was complete, excess of aniline was added, and the mixture was allowed to stand at room temperature for one hour. Water was added, and the ether layer was separated, washed successively with 10% hydrochloric acid, 10% sodium carbonate solution, and water, and then dried. The ether was distilled off, and the crystalline residue was washed on the filter with a mixture of diethyl ether and petroleum ether (1:4) (0.4 g of crystals, m.p. 125-129°). After crystallization from ether, the trans-anilide (XXXII) was obtained in the form of needles, m.p. 133-134°.

Found %: N 5.15, 5.34
$C_{16}H_{19}O_3N$. Calculated %: N 5.30

b) The dimethyl ester of trans-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (XXVII) (6 g) was added to a solution of 1.7 g of caustic potash in 25 ml of water and 90 ml of methanol, and the mixture was boiled for ten hours. Methanol was distilled off under reduced pressure, and the residual solution was extracted with ether to remove unhydrolyzed diether (1.8 g). The aqueous solution was treated with charcoal and filtered, and then acidified with hydrochloric acid. A liquid hydrolysis product separated, and this partially crystallized on standing. The crystalline product was filtered off and washed with petroleum ether, yielding 2.3 g of the trans-monoester (XXVIII), m.p. 71-75°. The liquid part, after extraction with ether, removal of ether, and treatment of the residue with petroleum ether, yielded a further 0.15 g of the crystalline trans-monoester (XXVIII), m.p. 71-74° (total yield 63%). After crystallization from petroleum ether, the product melted at 73-74°.

carboxy[1]-Monomethyl Ester of trans-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XXIX). a) A solution of the carboxy[1]-monomethyl ester of trans-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (XXVIII, 1.5 g), m.p. 73-74°, in 15 ml of absolute methanol was treated with hydrogen in presence of a Pd catalyst. One molecule of hydrogen (185 ml at 750 mm and 16°) was absorbed. When the solvent was distilled off, the hydrogenation product was caused to solidify by treatment with petroleum ether, and was recrystallized from a mixture of benzene and petroleum ether (1:5), yielding 1.35 g of the trans-monoester XXIX, m.p. 92-93°, which is in accord with data in the literature [2].

Found %: C 59.73; 59.74; H 7.92; 8.02
$C_{10}H_{16}O_4$. Calculated %: C 60.0 H 8.05

Anilide: The trans-monoester XXIX (0.3 g) was treated in the usual way with phosphorus pentachloride and aniline in ether solution, and 0.2 g of a crystalline product was obtained, which melted, after recrystallization from 40% methanol, at 103-105° and corresponded in analysis to the normal trans-anilide (XXXIII).

Found %: C 69.89; H 7.87; N 5.23
$C_{16}H_{21}O_3N$. Calculated %: C 69.80; H 7.70; N 5.08

b) The anhydride of trans-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (XXVI, 1.3 g) was added slowly to a solution of 0.35 g of sodium in 12 ml of absolute methanol, and the solution was boiled in a water bath for 30 minutes. Water (10 ml) was added, methanol was distilled off under reduced pressure, and the aqueous solution was treated with charcoal, filtered, and acidified with hydrochloric acid. When the mixture was cooled and allowed to stand, the liquid reaction product completely crystallized, it was filtered off, and washed with water and with petroleum ether (1.2 g, i.e., 77%; m.p. 86-92°). After crystallization from a mixture of benzene and petroleum ether, it melted at 91-93° and was found to be identical with the trans-monoester XXIX obtained previously (above).

c) The dimethyl ester of trans-1-methyl-1,2-cyclohexanedicarboxylic acid (XXXI, 9.4 g) was added to a solution of 2.8 g of caustic potash in 42 ml of water and 115 ml of methanol, and the mixture was boiled for ten hours. Methanol was removed under reduced pressure, and the residue was extracted with ether to remove unhydrolyzed

diester (2.1 g), treated with charcoal and filtered and acidified. The crystalline product was filtered off and washed with water and with petroleum ether (5.1 g, i.e., 75% on the amount of trans-diester hydrolyzed, of the trans-monoester XXIX; m.p. 85-90°). After crystallization from a mixture of benzene and petroleum ether, the pure trans-monoester melted at 92-93.5°.

Reaction of the Anhydride of trans-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXVI) with Methanol. A solution of 4 g of the trans-anhydride XXVI in 15 ml of absolute methanol was boiled in a water bath for four hours. After removal of methanol under reduced pressure, a viscous noncrystallizing reaction product was obtained, and this was dissolved in a small amount of warm petroleum ether and set aside at room temperature overnight with addition of seeding crystals of the trans-monoester XXVIII. Crystals (0.15 g) of m.p. 73-75° appeared; they were identical with the trans-monoester XXVIII. From the mother liquor, on long standing (10-15 days) a nonhomogeneous crystalline product (3.2 g, m.p. 43-55°) gradually separated. Fractional crystallization from petroleum ether yielded 0.2 g of the pure trans-monoester XXVIII and 1.2 g of another substance, which crystallized in the form of fine needles, m.p. 56-58°, and corresponded in alaysis to the isomeric trans-monoester XXXIV.

Found %: C 60.72; 60.76; H 7.17; 7.28
$C_{10}H_{14}O_4$. Calculated %: C 60.6 H 7.12

Anilide: The anilide of the trans-monoester XXXIV was obtained in the usual way. It melted, after crystallization from ether, at 112-114°, and it corresponded in composition to the normal trans-anilide (XXXV).

Found %: N 5.02; 5.30
$C_{16}H_{19}O_3N$. Calculated %: N 5.30

When the trans-monoester XXXIV was hydrogenated in methanol in presence of a Pd catalyst, a saturated liquid trans-monoester was obtained. This was converted into an anilide in the usual way, and the product, crystallized from a mixture of diethyl ether and petroleum ether, melted at 98-99° and corresponded in composition to the normal trans-anilide (XXXVI).

Found %: N 5.14; 5.07
$C_{22}H_{27}O_3N$. Calculated %: N 5.08

Acid Chloride of the carboxy[1]-Monomethyl Ester of trans-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXXVII). Oxalyl chloride (10 ml) was added to a solution of 8.5 g of the trans-monoester XXVIII in 70 ml of absolute benzene. The solution was set aside at room temperature overnight and then heated at 40° for 30 minutes. Benzene was distilled off, and the residue was a vacuum-distilled, yielding 8.7 g of the trans-acid chloride XXXVII, b.p. 104-105° (4 mm); n_D^{22} 1.4880.

Found %: Cl 16.55; 16.61
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.35

With aniline in ether solution the acid chloride XXXVII gave the pure trans-anilide (XXXII), m.p. 133-134°.

Acid Chloride of the carboxy[1]-Monomethyl Ester of trans-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XL). Oxalyl chloride (7 ml) was added to a solution of 6.6 g of the trans-monoester XXIX in 60 ml of absolute benzene, and the solution was set aside at room temperature for two hours. The solvent was distilled off, and the residue was vacuum-distilled, yielding 6.9 g of the trans-acid chloride XL, b.p. 96-97° (1.5 mm); n_D^{22} 1.4770.

Found %: Cl 16.35; 16.26
$C_{10}H_{15}O_3Cl$. Calculated %: Cl 16.17

With aniline in ether solution it gave the normal anilide, m.p. 104-105°, identical with the trans-anilide XXXIII.

trans-6-Carboxy-6-methyl-3-cyclohexene-1-acetic Acid (XXXVIII). A solution of 3 g of the trans-acid chloride XXXVII in 20 ml of absolute ether was added slowly to a cooled stirred dry ethereal solution of 2.5 g of diazomethane, and the mixture was set aside at room temperature overnight. Ether was removed under reduced pressure, and the crystalline residue of diazo ketone was dissolved with cooling in 60 ml of absolute methanol. Freshly prepared silver oxide (0.8 g) was added, and the mixture was boiled for eight hours. The solution was treated with charcoal and filtered, methanol was removed under reduced pressure, and the liquid residue was hydrolyzed with 15 ml of 40% caustic potash and 10 ml of methanol at the boil for four hours. The solution was treated with charcoal and filtered, methanol was distilled off under reduced pressure, and the aqueous solution was acidified with hydrochloric acid. The crystalline product was filtered off and washed carefully with water (2.35 g, i.e., 85.5%; m.p. 193-197°). Two crystallizations from acetone yielded pure trans-6-carboxy-6-methyl-3-cyclohexene-1-acetic acid (XXXVIII) having a constant melting point of 205-206°.

Found %: C 60.73; 60.75; H 7.10; 7.23

$C_{10}H_{14}O_4$. Calculated %: C 60.6 H 7.12

trans-2-Carboxy-2-methlcyclohexaneacetic Acid (XXXIX). a) An ethereal solution of 2.0 g of the trans-acid chloride XL was added slowly to a cooled dry ethereal solution of diazomethane prepared from 10 g of methylnitrosourea , and the mixture was set aside at room temperature overnight. Ether was removed under reduced pressure, and the crystalline diazo ketone (m.p. 42-44°) was dissolved in 40 ml of cold absolute methanol; 0.6 g of silver oxide was added, and the mixture was boiled for six hours. Methanol was distilled off, and the liquid product was hydrolyzed with 10 ml of 40% caustic potash and 5 ml of methanol at the boil for five hours. The solution was filtered and acidified with hydrochloric acid. A semisolid product was precipitated, and this was filtered off and washed with water and a mixture of acetone and petroleum ether (1:5). The product, 0.8 g of a crystalline acid, m.p. 175-177°, was pure trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX) [2].

Found %: C 60.07; 60.32; H 8.35; 8.25

$C_{10}H_{16}O_4$. Calculated %: C 60.0 H 8.05

The aqueous mother liquor and washings were evaporated to dryness under reduced pressure and extracted with acetone. Removal of acetone and treatment of the residue with petroleum ether yielded a further 0.2 g of the trans-acid, m.p. 165-175°, and this, after crystallization from a mixture of acetone and petroleum ether (1:2) melted at 176-177°. The total yield was 60%.

b) A solution of 0.8 g of trans-6-carboxy-6-methyl-3-cyclohexene-1-acetic acid (XXXVIII) in 20 ml of absolute methanol was hydrogenated over a Pd catalyst, and one molecule of hydrogen was absorbed. The solvent was distilled off, and the hydrogenation product was washed on the filter with a mixture of diethyl ether and petroleum ether (1:2), and yielded 0.75 g of pure trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX), m.p. 175-177°, identical with the product obtained in the first experiment.

SUMMARY

1. The crystalline cis-monoester VII and the liquid cis-monoester IX have been prepared from the cis-anhydride VI, the cis-dicarboxylic acid VIII, and the ester of this acid (X). By hydrogenation of these monoesters the corresponding saturated cis-monoesters XI and XIII have been prepared, and the structures of these have been proved by converting them into the known cis-carboxymethyl cyclohexaneacetic acids XVI and XX.

2. It has been found that, when the unsaturated cis-monoesters VII and IX and their acid chlorides XIV and XVIII react with aniline at 30°, the same product, the phenylimide XXIII, is obtained in all cases. Only under very mild reaction conditions (0°) was it possible to isolate the corresponding cis-anilides (XXIV and XXV), readily converted when heated with phosphoryl chloride into the phenylimide XXIII.

3. In the case of the cis-acid chlorides XVII and XXI, lengthening of the carbon chain occurs with partial conversion to the corresponding trans-acids XXXVIII and XXXIX. The secondary carboxy group enters into the Arndt-Eistert reaction considerably more readily than the tertiary carboxyl group.

4. The trans-monoester XXVIII, hydrogenation of which gives the saturated trans-monoester XXIX, was prepared in satisfactory yield from the trans-anhydride XXVI and the trans-diester XXVII.

5. The monoester and acid chlorides of the trans series readily give stable anilides, and they enter the Arndt-Eistert reaction considerably more readily than do the monoesters of the cis series.

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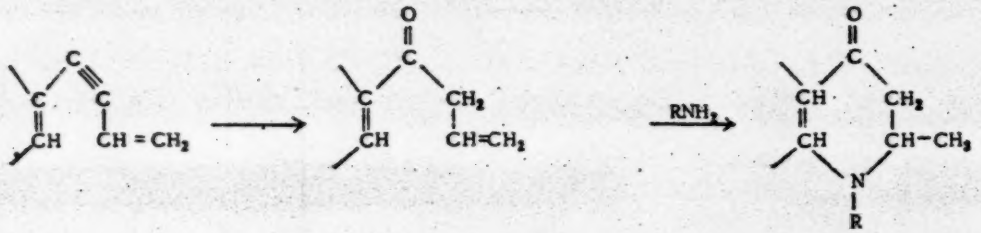
HETEROCYCLIC COMPOUNDS

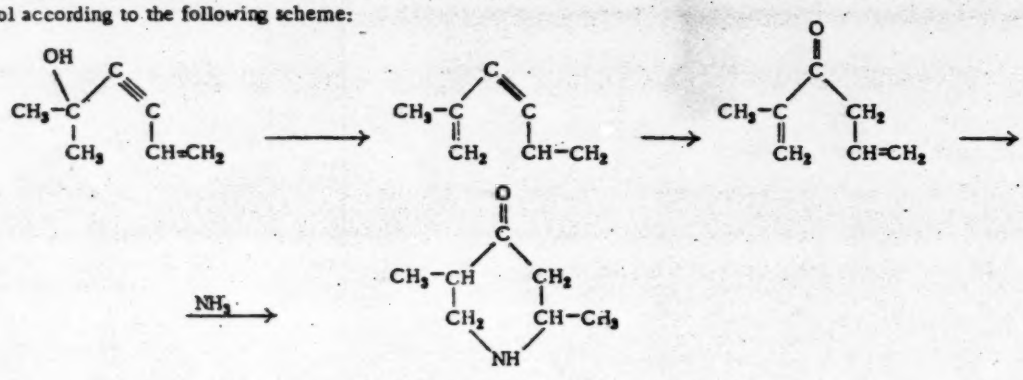
COMMUNICATION XXIX. STEREOISOMERISM OF 2,5-DIMETHYL-4-PIPERIDINOL, 1,2,5-TRIMETHYL-4-PIPERIDINOL, AND THEIR DERIVATIVES*

I. N. Nazarov, D. V. Sokolov, and V. N. Rakcheeva

Some years ago, Nazarov and his coworkers developed a new simple method for the preparation of various 4-piperidones by the use of acetylene [1]:

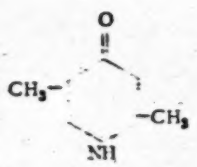


The discovery of this method, which made a very great variety of 4-piperidones readily accessible, enabled investigations into the synthesis of compounds of the piperidine series to be greatly extended and has led to the discovery of very valuable new medicinals having a sedative action (substitutes for morphine). The physiological activity of these compounds is generally greatly dependent not only on the number, disposition, and nature of the substituents in the piperidine ring, but also on their spatial arrangement. Investigations into the stereochemistry of piperidine derivatives are, therefore, not only of theoretical; but also of practical interest; and their importance is increased by the fact that this field has received very little study. As our starting substance for these stereochemical investigations we selected 2,5-dimethyl-4-piperidone (I), which is readily prepared from 2-methyl-5-hexen-3-yn-2-ol according to the following scheme:

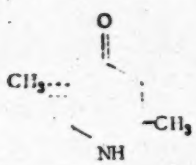


(I)

The piperidone I, having two asymmetric carbon atoms, may exist in two racemic forms, cis and trans:



cis form



trans form

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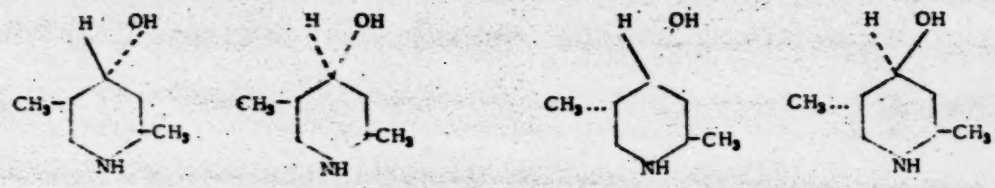
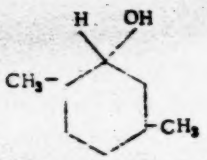
All attempts, however, to separate these piperidones, or their derivatives, have resulted in the isolation of only one form, probably the trans-form, of the piperidone I; it was not found possible to isolate the other isomer. When the carbonyl group of the piperidone I was reduced, 2,5-dimethyl-4-piperidinol (II) was formed, and this now has three asymmetric carbon atoms and may exist in four racemic forms corresponding to the following spatial dispositions of substituents:



cis series

trans series.

By the detailed investigation of the methods of reducing the piperidone I, we succeeded in isolating three of four theoretically possible racemates of 2,5-dimethyl-4-piperidinol (II), the melting points of which, and also of their picrates and hydrochlorides, are given below:

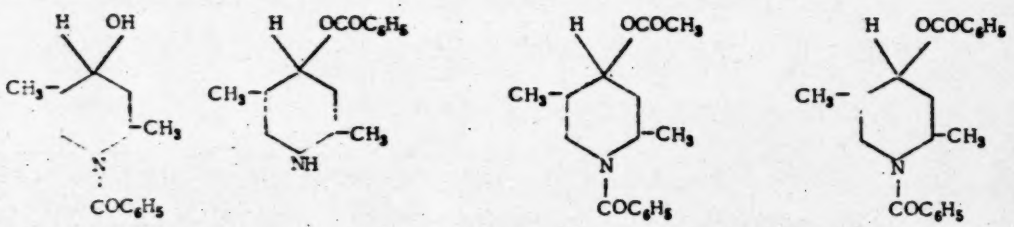


(II)

	Base	Picrate	Hydrochloride
α-Form	98°	174°	223°
β-Form	142°	180°	210°
γ-Form	87°	oil	188°

The α-form of the piperidinol II (m.p. 98°) is most readily obtained by reduction of the piperidone I by means of sodium and alcohol [2]. The β-form of the piperidinol II (m.p. 142°) is most simply prepared by hydrogenation of the piperidone I in presence of a nickel catalyst [2]. The γ-form of the piperidinol II is most readily isolated by hydrogenation of the benzoyl or acetyl derivative of the piperidone I in presence of a nickel catalyst, followed by elimination of the acyl group on the nitrogen by means of hydrochloric acid. When the β- and γ-forms of the piperidinol II were heated with sodium isopentyloxide [3], they were isomerized into the more stable α-form, m.p. 98°, which is probably one of the epimers of the trans series. The missing fourth stereoisomer of the piperidinol II must, therefore, be one of the epimers of the unstable cis series.

The simple methods that we have developed for the preparation of three stereoisomers of the piperidinol II have made it possible to make a detailed investigation of their properties and reactions. In particular, we have synthesized the following benzoyl and acetyl derivatives of the α-, β-, and γ-isomers of the piperidinol II, and we give their melting points in Table 1:



(III)

(IV)

(V)

(VI)

TABLE 1

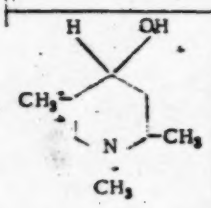
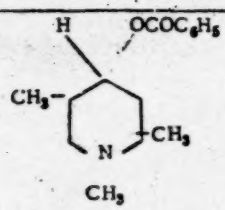
	α-Form	β-Form	γ-Form
III	137°	135°	160°
IV	Picrate 195°; Hydrochloride 266°	Picrate 230°, Hydrochloride 168°	Picrate 174°; Hydrochloride 254°
V	Oil	120°	93°
VI	93°	93°	118°

Although the benzoyl derivatives of the α- and β-forms of III and VI have identical melting points, these are greatly depressed in mixture tests, and there can be no doubt that they are different substances.

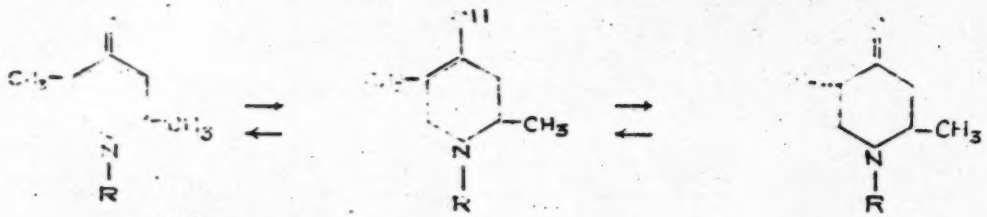
The benzoyl derivatives III were readily prepared in high yield (about 90%) by the action of benzoyl chloride on the piperidinols II in presence of alkali. The benzoic esters IV were prepared by heating benzoyl chloride with the hydrochlorides of the piperidinols II at 140-150°. The mixed diacyl derivatives V were prepared by acetylation of the benzoyl derivatives III with acetic anhydride, and the dibenzoyl derivatives VI were obtained by benzoylation of the monobenzoyl derivatives III or IV with benzoyl chloride.

Methylation of the isomeric 2,5-dimethyl-4-piperidinols (II) by means of a mixture of formaldehyde and formic acid [4] yielded the α-, β-, and γ-forms of 1,2,5-trimethyl-4-piperidinol (VII), the hydrochlorides of which were converted by heating with benzoyl chloride into the corresponding benzoic esters (VIII). The melting points of these compounds, their picrates, and their hydrochlorides are given in Table 2.

TABLE 2

	Melting point (°C)					
	 (VII)			 (VIII)		
	Base	Picrate	Hydrochloride	Base	Picrate	Hydrochloride
α-Form	73	143	196	Liquid	200	202
β-Form	78	183	Oil		218	Oil
γ-Form	Liquid	168			182	179

When the α-, β-, and γ-forms of 2,5-dimethyl-4-piperidinol (II) are oxidized with chromic acid, the same 2,5-dimethyl-4-piperidone (I) (picrate, m.p. 168-169°) is obtained in each case. This isomer of the piperidone I probably belongs to the trans series, and it would appear that the second isomer (cis), which cannot be isolated, is formed only as a stage in the reaction (of the reduction or hydrogenation of the carbonyl group). It is quite possible, therefore, that, under the conditions of reduction or catalytic hydrogenation, the piperidone I and its N-derivatives may undergo reversible cis-trans isomerization:

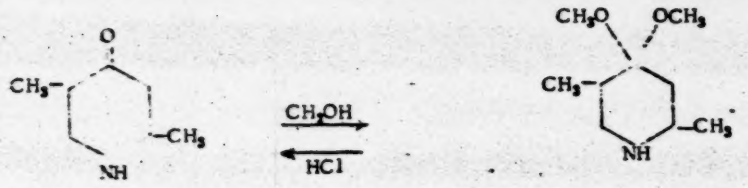


Similar transformations may occur also under the action of organometallic compounds (RMgX, RLi), and also in the condensation of 4-piperidones with acetylene in presence of caustic potash, sodamide, or sodium in liquid ammonia.

In a careful investigation of the conditions required for the formation of picrates of the piperidone I, we established that a component ratio of 1:1 led to the formation of the normal picrate, m.p. 169° (large yellow rods), and that in presence of an excess of the piperidone I a picrate of m.p. 138° (yellow needles) was formed, which contained one molecule of picric acid for each two molecules of the piperidone The picrates are interconvertible:

$$\text{Picrate, m.p. 169°} \xrightarrow[\text{picric acid}]{\text{piperidone I}} \text{Picrate, m.p. 138°}$$

When the piperidone I was treated with a hot methanolic solution of an equimolecular proportion of picric acid, together with the ordinary picrate (m.p. 169°), the picrate of the dimethyl ketal (IX), m.p. 122-123°, was obtained also. Decomposition of this picrate with an aqueous solution of potassium carbonate yielded the free dimethyl ketal (IX), and this was hydrolyzed with dilute hydrochloric acid with formation of methanol and the piperidone I:



The hydrochlorides of the α-, β-, and γ-forms of the benzoic esters IV and VIII were tested for their anesthetic activity. The results of these tests are given in Table 3.

TABLE 3

Conc. of soln. (%)	Anesthetic activity in Renier units (average values)*						Novocaine
	Benzoic esters IV			Benzoic esters VIII			
	α	β	γ	α	β	γ	
0.25	223	269	569	343	409	295	109
0.5	474	492	815	544	693	588	181
1.0	629	376	924	721	1089	700	255
2.0	594	861	1106	933	812	1010	309

As will be seen from Table 3, some of the compounds were found to be considerably more active (100-200%) as local anesthetics than novocaine. However, owing to their high toxicity and irritative action, they are not of practical importance.

* The tests were carried out in the Pharmacology Department of the V. M. Molotov Kazakhstan Medica Institute by Gordin, Samarina, and Chebekova.

EXPERIMENTAL

The 2,5-dimethyl-4-piperidone (I) used in this work was prepared by the previously described method and had the following constants: b.p. 78° (7 mm); n_D^{20} 1.4660.

Reduction of 2,5-Dimethyl-4-piperidone with Sodium in Alcoholic Solution (α-Form of 2,5-Dimethyl-4-piperidinol, m.p. 97-98°)

A solution of 12.7 g of 2,5-dimethyl-4-piperidone (I) in 350 ml of absolute alcohol was prepared in a flask fitted with mechanical stirrer, and it was stirred continuously while 35 g of sodium was added in small pieces. Toward the end of the reaction the liquid, which had become viscous, was warmed until the whole of the sodium had dissolved. When cool, the reaction mixture was diluted with 100 ml of water and acidified with hydrochloric acid. The precipitated sodium chloride was filtered off, and the alcohol and much of the water weredriven off under somewhat reduced pressure. The viscous residue was transferred to a separating funnel and treated with solid caustic soda. The free base was carefully extracted with ether, the extract was dried with potassium carbonate, the ether was removed, and the residue was vacuum-distilled, yielding the piperidinol (b.p. 101-102°/ 8mm), which crystallized in the receiver. The crystals were pressed off at the pump, washed three times with small portions of ether, and recrystallized from gasoline (b.p. 120-150°), yielding 7.3 g of the α-form of 2,5-dimethyl-4-piperidinol (II), m.p. 97-98°.

Found %: N 10.81; 10.90

$C_7H_{15}ON$. Calculated %: N 10.85

The picrate was prepared by dissolving 0.5 g of the piperidinol in 30 ml of a saturated methanolic solution of picric acid; it was obtained in the form of rods, m.p. 173-174° (from methanol).

Found %: N 15.77; 15.80

$C_{13}H_{18}O_8N_4$. Calculated %: N 15.64

The hydrochloride was prepared by the action of hydrogen chloride on the piperidinol in alcoholic solution, followed by precipitation with ether; it formed crystals of m.p. 222-223°.

From the ether mother liquors, containing a mixture of noncrystallizing piperidinols, after removal of ether and benzoylation with benzoyl chloride in presence of alkali in the cold, about 1 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 160°) was obtained. It showed no melting-point depression with an authentic sample (see below).

Hydrogenation of 2,5-Dimethyl-4-piperidone in Presence of a Nickel Catalyst (β-Form of 2,5-Dimethyl-4-piperidinol, m.p. 142°

A solution of 20.7 g of the piperidone I in 100 ml of alcohol was treated with hydrogen in presence of 1.5 g of Raney nickel and 0.5 ml of 20% caustic soda. After 20 hours' shaking, 4.1 liters of hydrogen had been absorbed, against 4.3 liters required by theory. The catalyst was filtered off, alcohol was distilled off under somewhat reduced pressure until a dry crystalline residue was obtained, and the residue was washed with ether and recrystallized from gasoline (b.p. 80-100°), yielding 4.1 g of the β-form of 2,5-dimethyl-4-piperidinol (II), m.p. 141-142°, in the form of light scalelike leaves.

Found %: N 10.76; 10.90
$C_7H_{15}ON$. Calculated %: N 10.85

The picrate was prepared by dissolving the piperidinol in a saturated methanolic solution of picric acid. It formed polyhedral prisms, m.p. 179-180° (from methanol). In admixture with the above-described picrate of the α-form (m.p. 173-174°) it melted at 142-146°.

Found %: N 15.90; 15.80
$C_{13}H_{18}O_8N_4$. Calculated %: N 15.64

The hydrochloride formed crystals of m.p. 209-210° (reprecipitated from alcohol).

From the mixture of isomeric piperidinols (16.4 g) remaining after separation of the β-form of m.p. 141-142°, 10.5 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III) was obtained by the action of benzoyl chloride in the cold in presence of caustic soda. It melted at 159-160°, and the melting point was not depressed by an authentic sample (see below).

Electrolytic Reduction of 2,5-Dimethyl-4-piperidone

Reduction was carried out at a lead cathode (10.5 cm x 11.2 cm) at a current density of 0.029 amp per sq cm at 20° in a 10% solution of ammonium sulfate [3]. The cathode space was separated from the anode by means of a porous pot. The current was switched on, and 20 ml of the piperidone I was added to the cathode department, when evolution of hydrogen stopped. The reduction was discontinued after five hours (theoretically, 2 hours 30 minutes was required). The cathode solution was transferred to a Claisen flask, acidified with hydrochloric acid, and evaporated almost to dryness under reduced pressure. Excess of solid caustic soda was added to the residue, and the liberated base was extracted with several portions of hot gasoline (b.p. 80-100°). When the gasoline solution stood overnight, 2.2 g of crystals were precipitated, and these, after recrystallization, melted at 141-142° and showed no melting-point depression in admixture with the β-form of 2,5-dimethyl-piperidinol obtained in the preceding experiment.

Benzoylation of 2,5-Dimethyl-4-piperidone

2,5-Dimethyl-4-piperidone (I, 30 g) and water (236 ml) were placed in a three-necked round-bottomed flask provided with a mechanical stirrer. Benzoyl chloride (50 g) and 15% caustic soda (100 ml) were added alternately in small portions under continuous stirring. The layer of viscous oil that formed was transferred to a separating funnel, washed with a 50% solution of caustic soda, and extracted with benzene. The benzene extract was dried with potassium carbonate, and the benzene was distilled off. Two vacuum distillations yielded 50 g of 1-benzoyl-2,5-dimethyl-4-piperidone in the form of a viscous oil, b.p. 192-193° (5 mm). On long standing, and also when rubbed with a glass rod, the oil crystallized completely, giving colorless crystals, m.p. 64-65° (from petroleum ether).

Found %: N 6.04; 6.03
$C_{14}H_{17}O_2N$. Calculated %: N 6.06

A solution of 0.47 g of 1-benzoyl-2,5-dimethyl-4-piperidone was mixed with a solution of 0.4 g of 2,4-dinitrophenylhydrazine and 1.4 ml of concentrated hydrochloric acid in 80 ml of alcohol. The mixture was heated for ten minutes in a water bath and then set aside for five days, when 0.35 g of the 2,4-dinitrophenylhydrazone was obtained (m.p. 211-212°, from a mixture of chloroform and alcohol).

Found %: N 17.09; 17.08

$C_{28}H_{32}O_3N_2$. Calculated %: N 17.00

Hydrogenation of 1-Benzoyl-2,5-dimethyl-4-piperidone

1-Benzoyl-2,5-dimethyl-4-piperidone (21.4 g, m.p. 64-65°) was hydrogenated as a solution in 120 ml of alcohol in presence of 0.5 ml of 20% caustic soda and 1.5 g of Raney nickel. The calculated amount of hydrogen (2500 ml) was absorbed when the flask had been shaken for six hours. The catalyst was filtered off, and the alkali was neutralized with a few drops of hydrochloric acid. Alcohol was then removed under reduced pressure, and the residue remaining in the flask crystallized completely.

Three further similar experiments were carried out, and in this way altogether 120 g of a crystalline mixture of isomers of 1-benzoyl-2,5-dimethyl-4-piperidinol (III) was obtained. From this mixture, by fractional crystallization from benzene, 47 g of the pure γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol, m.p. 159-160°, was obtained.

Found %: N 6.02; 6.09

$C_{14}H_{19}O_2N$. Calculated %: N 6.01

The phenylurethan melted at 178-179° (from gasoline).

Found %: N 8.08; 8.09

$C_{21}H_{24}O_3N_2$. Calculated %: N 7.96

The benzene mother liquor was evaporated down, and gasoline (b.p. 80-100°) was added, resulting in the separation of a further 30 g of crystals, m.p. 88-95°, which consisted mainly of a mixture of the α- and β-forms of 1-benzoyl-2,5-dimethyl-4-piperidinol.

Found %: N 6.05; 6.04

$C_{14}H_{19}O_2N$. Calculated %: N 6.01

Hydrolysis of 1-Benzoyl-2,5-dimethyl-4-piperidinol (γ-Form of 2,5-Dimethyl-4-piperidinol, m.p. 87°

A mixture of 10 g of the pure γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) and 100 ml of 18% hydrochloric acid was heated in a boiling water bath for 35 hours. The benzoic acid formed was filtered off, and the filtrate was evaporated to dryness and then treated with a 50% solution of caustic soda. The free base was extracted with ether, dried with potassium carbonate, and vacuum-distilled, yielding 4 g of the γ-form of 2,5-dimethyl-4-piperidinol (II), b.p. 82-84°/2 mm, which completely crystallized in the receiver. It melted, after two crystallizations from gasoline, at 86-87°.

Found %: N 10.71; 10.72

$C_7H_{15}ON$. Calculated %: N 10.85

The picrate formed a thick noncrystallizing oil. The hydrochloride was prepared by the action of hydrogen chloride on the piperidinol in methanol solution, followed by precipitation with dry ether (large needles, m.p. 187-188°).

When the mixture of isomers of 1-benzoyl-2,5-dimethyl-4-piperidinol of m.p. 88-95° was hydrolyzed in a similar way, the α- and β-forms of 2,5-dimethyl-4-piperidinol were isolated; they melted respectively at 98° and 142°, undepressed by addition of the above-described samples. The β-form (m.p. 142°) was precipitated directly from ether, and the α-form (m.p. 98°) was then separated from the mother liquors via the hydrochloride. Hence, in the hydrogenation of 1-benzoyl-2,5-dimethyl-4-piperidone in presence of a nickel catalyst, three isomeric forms (α, β, and γ) of 1-benzoyl-2,5-dimethyl-4-piperidinol (III) were formed.

Acetylation of 2,5-Dimethyl-4-piperidone with Acetic Anhydride

Acetic anhydride (36 g) was added with cooling and stirring to 37.2 g of 2,5-dimethyl-4-piperidone, and the solution obtained, which had become warm, was heated in a boiling water bath for 30 minutes. Acetic acid and excess of acetic anhydride were distilled off under reduced pressure, and the residue was washed with 50% caustic soda and extracted with benzene. The benzene extract was dried, and the benzene was removed. Vacuum distillation of the residue yielded 43 g of 1-acetyl-2,5-dimethyl-4-piperidone, b.p. 122-124° (3 mm); n_D^{20} 1.4913; d_4^{20} 1.0792; found MR 45.38; calculated MR 45.52. On standing, the substance solidified completely to crystals of m.p. 56-57° (from petroleum ether).

Found %: N 8.38; 8.31

$C_9H_{15}O_2N$. Calculated %: N 8.28 .

Acetylation of 2,5-Dimethyl-4-piperidone with Ketene

A current of gaseous ketene, prepared by the pyrolysis of acetone in a porcelain tube at 600-700°, was passed for two hours through a solution of 27.3 g of 2,5-dimethyl-4-piperidone in 50 ml of dioxane contained in a special acetylation apparatus. The acetylation product, after removal of dioxane, was vacuum-fractionated, yielding 34 g of 1-acetyl-2,5-dimethyl-4-piperidone, b.p. 117-118° (2 mm); n_D^{20} 1.4925; d_4^{20} 1.0816; found MR 45.41; calculated MR 45.52. On standing, the substance solidified completely to crystals of m.p. 56-57°, undepressed by the sample obtained in the preceding experiment. The 2,4-dinitrophenylhydrazone melted at 177-179° (from alcohol).

Found %: N 20.19; 20.03

$C_{15}H_{18}O_5N_5$ Calculated %: N 20.07

Hydrogenation of 1-Acetyl-2,5-dimethyl-4-piperidone

1-Acetyl-2,5-dimethyl-4-piperidone (10.3 g) was hydrogenated as a solution in 90 ml of alcohol in presence of 0.5 ml of 20% caustic soda and 2 g of Raney nickel. The calculated amount of hydrogen (1.68 liter) had been absorbed when the flask had been shaken for two hours. The catalyst was filtered off, the alcohol was driven off, and the residue was dissolved in benzene. The benzene solution was dried with potassium carbonate, and the residue remaining after removal of benzene was vacuum-distilled, yielding 9.4 g of a mixture of isomers of 1-acetyl-2,5-dimethyl-4-piperidinol in the form of a thick syrup, b.p. 135-138° (2 mm). Two further similar experiments were carried out, and altogether 30 g of hydrogenation products was obtained, and from this, on standing, 9 g of crystals of the pure γ-form of 1-acetyl-2,5-dimethyl-4-piperidinol was obtained in the form of long rods, m.p. 86-87° (from gasoline of b.p. 80-100°).

Found %: N 8.13; 8.19

$C_9H_{17}O_2N$. Calculated %: N 8.18

The phenylurethan melted at 232-233° (from benzene).

Found %: N 9.82; 9.76

$C_{16}H_{22}O_3N_2$ Calculated %: N 9.65

Hydrolysis of 1-Acetyl-2,5-dimethyl-4-piperidinol

A mixture of 5.6 g of the above-described γ-form of 1-acetyl-2,5-dimethyl-4-piperidinol (m.p. 86-87°) and 70 ml of 18% hydrochloric acid was heated in a boiling water bath for 30 hours. Acetic and hydrochloric acids were driven off under reduced pressure, and the residue was treated with 50% caustic soda solution. The base was extracted with ether, the ether extract was dried with potassium carbonate, and the residue after removal of ether was crystallized from gasoline (b.p. 80-100°), yielding 3 g of the γ-form of 2,5-dimethyl-4-piperidinol, m.p. 86-87°, undepressed by the substance obtained by the hydrolysis of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol, which is described above.

Isomerization of the β-Form of 2,5-Dimethyl-4-piperidinol

The β-form of 2,5-dimethyl-4-piperidinol (4 g, m.p. 141-142°) was boiled for 43 hours at 180-190° with a solution of sodium isopentyloxide obtained by dissolving 7 g of sodium in 50 ml of isopentyl alcohol. An equal volume of water was added to the hot solution, and the layer of alcohol that separated was washed six times with hydrochloric acid (1:1). The acid extracts were added to the water layer, which was then extracted with ether and evaporated to low bulk. The precipitated sodium chloride was filtered off and washed with hydrochloric acid. The mother liquor was evaporated under reduced pressure to a thick syrup and treated with 50% caustic soda. The base was extracted with ether, and the extract was dried with potassium carbonate. The residue after removal of ether was crystallized three times from gasoline (b.p. 120-150°), yielding 1.2 g of the α-form of 2,5-dimethyl-4-piperidinol, m.p. 96-98°, undepressed by the above-described sample.

Isomerization of the γ-Form of 2,5-Dimethyl-4-piperidinol

The γ-form of 2,5-dimethyl-4-piperidinol (4 g, m.p. 86-87°) was boiled for 46 hours with a solution of sodium isopentyloxide. The reaction product was treated as in the preceding experiment. After removal of ether, the base was vacuum-distilled, and yielded 1.1 g of crude product, b.p. 83-84° at 1.5 mm. Three crystallizations from gasoline yielded 0.4 g of crystals of the α-form of 2,5-dimethyl-4-piperidinol, m.p. 96-97°, undepressed by an authentic sample.

α-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Benzoyl chloride (2.2 g) was added to a cooled (ice water) solution of 2 g of the α-form of 2,5-dimethyl-4-piperidinol (II) (m.p. 97-98°) in 6 ml of water containing 0.6 g of caustic soda. The mixture was shaken vigorously until the odor of benzoyl chloride disappeared (30 minutes). The lumps that had formed were ground up, washed three times with water, and dried in a vacuum desiccator, yielding 2.6 g of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III), m.p. 136-137° (from a mixture of benzene and gasoline, 7:3).

Found %: N 6.23

$C_{14}H_{19}O_2N$. Calculated %: N 6.05

β-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Benzoylation of 2 g of the β-form of 2,5-dimethyl-4-piperidinol (II, m.p. 141-142°) by the above-described method yielded 2.65 g of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III), m.p. 134-135° (from a 1:1 mixture of benzene and gasoline).

Found %: N 6.01; 6.09

$C_{14}H_{19}O_2N$. Calculated %: N 6.05

A mixture test with the α-form (m.p. 136-137°) obtained in the preceding experiment showed a depression (m.p. 112-116°).

Benzoic Ester of the α-Form of 2,5-Dimethyl-4-piperidinol

A mixture of 5 g of the hydrochloride of the α-form of 2,5-dimethyl-4-piperidinol (m.p. 222°) and 8 g of freshly distilled benzoyl chloride was heated at 140-150° until hydrogen chloride ceased to be evolved (about one hour). The product was dissolved in water, extracted several times with ether, and treated with sodium carbonate. The liberated base was dissolved in ether, and the ether solution was dried with sodium sulfate. Removal of ether followed by vacuum distillation of the residue yielded 2.2 g of the benzoic ester of the α-form of 2,5-dimethyl-4-piperidinol (IV) in the form of a slightly yellowish liquid, b.p. 164-165° (6 mm); n_D^{20} 1.5240; d_4^{20} 1.0625; found MR 67.12; calculated MR 66.30.

Found %: N 6.16

$C_{14}H_{19}O_2N$. Calculated %: N 6.05

The picrate was obtained by mixing the benzoic ester with a saturated solution of picric acid in methanol: fine needles, m.p. 194-195° (from methanol).

Found %: N 12.5; 12.4

$C_{20}H_{22}O_9N_4$. Calculated %: N 12.12

The hydrochloride was obtained by precipitation from alcohol with ether: minute needles, m.p. 265-266°, moderately soluble in water, readily soluble in alcohol.

Benzoic Ester of the β-Form of 2,5-Dimethyl-4-piperidinol

A mixture of 3 g of the hydrochloride of the β-form of 2,5-dimethyl-4-piperidinol (m.p. 209-210°) and 3.2 g of benzoyl chloride was heated at 140-150°, as described above. The usual treatment yielded 2.5 g of the benzoic ester of the β-form of 2,5-dimethyl-4-piperidinol (IV) in the form of a yellowish liquid, b.p. 166° (7 mm); n_D^{20} 1.5250; d_4^{20} 1.0860; found MR 66.76; calculated MR 66.30.

Found %: N 6.26

$C_{14}H_{19}O_2N$. Calculated %: N 6.05

Picrate: long coarse needles, m.p. 235-236° (from methanol).

Found %: N 12.47; 12.29

$C_{20}H_{22}O_9N_4$. Calculated %: N 12.42

Hydrochloride: fine, matted needles, m.p. 167-168.5° (from a mixture of alcohol and ether), readily soluble in water and alcohol.

Benzoic Ester of the γ-Form of 2,5-Dimethyl-4-piperidinol

A mixture of 10 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) and 10 g of freshly distilled benzoyl chloride was heated at 170° until the evolution of hydrogen chloride ceased. A current of dry hydrogen chloride was then passed through the reaction mixture at the same temperature for two hours. The

precipitated hydrochloride was washed with benzene and dissolved in a small amount of water. The hydrochloride was decomposed with a saturated solution of sodium carbonate, and the liberated base was extracted with ether. The ether extract was dried with sodium sulfate and the ether was driven off. Vacuum distillation of the residue yielded 5.5 g of the benzoic ester of the γ-form of 2,5-dimethyl-4-piperidinol (IV) in the form of a colorless liquid, b.p. 125-126° (1 mm); n_D^{20} 1.5265; d_4^{20} 1.0633; found MR 67.3; calculated MR 66.3.

Found %: N 5.83
$C_{14}H_{19}O_2N$. Calculated %: N 6.05

Picrate: fine convex rosettes, m.p. 173-174.5° (from methanol).

Found %: N 12.13; 12.16
$C_{20}H_{22}O_9N_4$. Calculated %: N 12.12

Hydrochloride: fine needles, m.p. 253-254° (precipitation from alcohol with ether), soluble in water and alcohol.

Benzoic Ester of the α-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

A mixture of 2 g of the benzoic ester of the α-form of 2,5-dimethyl-4-piperidinol (IV), 5 ml of 10% caustic soda, and 1.8 g of freshly distilled benzoyl chloride was cooled with ice water and shaken until the odor of benzoyl chloride disappeared. The thick mass was washed by grinding it with a 10% sodium carbonate solution and then with water, and it was dried in a vacuum desiccator. Three crystallizations from gasoline (b.p. 80-100°) yielded 2 g of the benzoic ester of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (VI) in the form of large rods, m.p. 92-93°.

Found %: N 4.14
$C_{21}H_{23}O_2N$. Calculated %: N 4.15

Benzoic Ester of the β-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

From 3 g of the benzoic ester of the β-form of 2,5-dimethyl-4-piperidinol (IV), the above-described procedure yielded 4.2 g of the benzoic ester of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (VI) in the form of long wide plates, m.p. 92-93° (from gasoline).

Found %: N 4.13
$C_{21}H_{23}O_2N$. Calculated %: N 4.15

Benzoic Ester of the γ-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

A mixture of 3 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) and 5 g of benzoyl chloride was boiled in benzene solution for 24 hours. The residue remaining after removal of benzene under reduced pressure was crystallized from a mixture of benzene and gasoline. The first crop consisted of 0.5 g of the starting material, m.p. 159-160°. After some evaporation, a precipitate of 2.5 g of the benzoic ester of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (VI), m.p. 117-118° (from gasoline/benzene 7:3), was obtained.

Found %: N 4.13; 4.04
$C_{21}H_{23}O_2N$. Calculated %: N 4.15

Acetic Ester of the α-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

A mixture of 2 g of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 136-137°) and 4 g of acetic anhydride containing one drop of concentrated sulfuric acid was heated at 60° for 7 hours 30 minutes. The excess of acetic anhydride was distilled off under reduced pressure, and the product was washed with a saturated sodium carbonate solution and extracted with ether. The ether extract was dried with calcined sodium sulfate. Vacuum fractionation yielded 2.5 g of the acetic ester of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (V) in the form of a viscous oil, b.p. 187-189° (2 mm); n_D^{20} 1.5290.

Found %: N 5.13
$C_{16}H_{21}O_3N$. Calculated %: N 5.09

Acetic Ester of the β-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Acetylation of 1.3 g of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 134-135°) by the above-described method yielded 1.4 g of the acetic ester of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (V), m.p. 125-126° (from gasoline).

Found %: N 5.24
$C_{15}H_{21}O_3N$. Calculated %: N 5.09

Acetic Ester of the γ-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Acetylation of 5 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) with 10 g of acetic anhydride by the method described above yielded 5 g of the acetic ester of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (V), m.p. 92.5-93° (from gasoline).

Found %: N 5.07, 5.26
$C_{16}H_{21}O_3N$. Calculated %: N 5.09

α-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 3.8 g of 32% formaldehyde, 2.2 g of 90% formic acid, and 5 g of the α-form of 2,5-dimethyl-4-piperidinol (II, m.p. 97-98°) was boiled under reflux in a water bath until evolution of carbon dioxide ceased (6 hours 20 minutes). The cooled solution was treated with solid caustic soda, and the base was extracted with ether. The ether extract was dried with calcined potassium carbonate. Vacuum fractionation yielded 4.7 g of the α-form of 1,2,5-trimethyl-4-piperidinol (VII), b.p. 87-89° (4 mm); n_D^{20} 1.4730; d_4^{20} 0.9541; Found MR 42.13; Calculated MR 42.41. This substance is rather viscous liquid; it crystallizes completely on standing, oblong leaves, m.p. 72-73°).

Found %: N 9.74
$C_9H_{17}ON$. Calculated %: N 9.78

Picrate: fine needles grouped together in starlike clusters, m.p. 142-143° (from methanol). Hydrochloride: m.p. 195-196° (precipitated by ether from alcohol).

β-Form of 1,2,5-Trimethyl-4-piperidinol

Methylation of 5 g of the β-form of 2,5-dimethyl-4-piperidinol (II, m.p. 141-142°) by the above-described procedure yielded 4.3 g of the β-form of 1,2,5-trimethyl-4-piperidinol (VII), m.p. 77-78°: long plates, soluble in water and organic solvents.

Found %: N 9.77
$C_9H_{17}ON$. Calculated %: N 9.78

Picrate: fine, matted needles, m.p. 181-182°. Hydrochloride: hygroscopic crystals, deliquescing in air.

Benzoic Ester of the α-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 4.5 g of the hydrochloride of the α-form of 1,2,5-trimethyl-4-piperidinol (m.p. 196°) and 6 g of freshly distilled benzoyl chloride was heated at 150° until evolution of hydrogen chloride ceased (20-30 minutes). The cooled thick mass was dissolved in water, extracted three times with ether, and decomposed with a saturated solution of sodium carbonate. The base, which floated on the surface, was extracted with ether, and the ether extract was dried with potassium carbonate and vacuum-distilled, yielding 5.2 g of the benzoic ester of the α-form of 1,2,-5-trimethyl-4-piperidinol (VIII) in the form of an almost colorless oil, b p. 135-136° (2 mm); n_D^{20} 1.5170; d_4^{20} 1.0315; Found MR 72.22; Calculated MR 71.26.

Found %: N 5.45
$C_{15}H_{21}O_2N$. Calculated %: N 5.67

Picrate: needles, m.p. 199-200° (from methanol).

Found %: N 12.26, 12.19
$C_{21}H_{24}O_9N_4$. Calculated %: N 11.76

Hydrochloride: large needles, formed into clusters, m.p. 201-202° (precipitated by ether from alcohol); readily soluble in water and alcohol.

Benzoic Ester of the β-Form of 1,2,5-Trimethyl-4-piperidinol

Benzoylation of 6 g of the hydrochloride of the β-form of 1,2,5-trimethyl-4-piperidinol (m.p. 182°) by the above-described procedure yielded 8.5 g of the benzoic ester of the β-form of 1,2,5-trimethyl-4-piperidinol (VIII) in the form of an oil, b.p. 128-130° (2 mm); n_D^{20} 1.5190; d_4^{20} 1.0440; Found MR 71.8; Calculated MR 71.26

Found %: N 5.9
$C_{15}H_{21}O_2N$. Calculated %: N 5.67

Picrate: fine needles, m.p. 217-218° (from methanol).

Found %: N 12.03, 11.95
$C_{21}H_{24}O_9N_4$. Calculated %: N 11.76

Hydrochloride: thick noncrystallizing mass.

Benzoic Ester of the γ-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 4.55 g of the benzoic ester of the γ-form of 2,5-dimethyl-4-piperidinol (IV), 1.88 g of 32% formaldehyde, and 1 g of 90% formic acid was heated in a boiling water bath until evolution of carbon dioxide ceased (40 minutes). The product was washed with sodium carbonate and extracted with ether; the ether extract was dried with sodium sulfate. Vacuum distillation yielded 4.1 g of the benzoic ester of the γ-form of 1,2,5-trimethyl-4-piperidinol (VIII) in the form of a colorless oil, b.p. 136-137° (2.5 mm); n_D^{20} 1.5195; d_4^{20} 1.0399; Found MR 72.15; Calculated MR 71.26.

	Found %:	N 6.77
$C_{15}H_{21}O_2N$.	Calculated %:	N 5.67

Picrate: fine square plates, m.p. 181-182° (from methanol). Hydrochloride (precipitated with ether from alcohol): crystals, m.p. 178-179.5°, readily soluble in water and alcohol.

γ-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 3.15 g of the benzoic ester of 1,2,5-trimethyl-4-piperidinol (VIII) and 40 ml of 25% hydrochloric acid was heated in a boiling water bath for two hours. Benzoic acid was filtered off, and the mother liquor was evaporated and treated with caustic soda. The base was extracted with ether, and the ether extract was dried with potassium carbonate. Vacuum distillation yielded 1.1 g of the γ-form of 1,2,5-trimethyl-4-piperidinol (VII) in the form of a liquid, b.p. 88° (6 mm).

	Found %:	N 9.70, 9.71
$C_8H_{17}ON$.	Calculated %:	N 9.78

Picrate: small oblong plates, m.p. 167-168° (from methanol).

	Found %:	N 14.94, 14.93
$C_{14}H_{20}O_8N_4$.	Calculated %:	N 15.05

Hydrochloride: hygroscopic mass that did not readily crystallize.

Picrates of 2,5-Dimethyl-4-piperidone (I)*

a) Equimolecular proportions of 2,5-dimethyl-4-piperidinol (0.5 g) and picric acid (0.9 g) were dissolved in 5 ml of methanol. After some evaporation, followed by cooling, 1.04 g of a picrate was precipitated in the form of large yellow rods, m.p. 168-169°. The evaporated mother liquid, on standing, yielded a further 0.24 g of a picrate having the same melting point. Altogether, therefore, 1.3 g (93%) was obtained. The picrate was very soluble in methanol.

	Found %:	C 43.33, 43.49;	H 4.70, 4.63;	N 15.85, 15.73
$C_{13}H_{16}O_8N_4$.	Calculated %:	C 43.84;	H 4.53;	N 15.73

When this picrate (20 g) was decomposed with aqueous potassium carbonate, the product was the piperidone (I), b.p. 16-17°; n_D^{20} 1.4656; d_4^{20} 0.9745; Found MR 36.07; Calculated MR 35.96. The above-described picrate of m.p. 168-169° (1.4 g) was dissolved by heating it with 5 ml of methanol, and one molecular proportion (0.5 g) of 2,5-dimethyl-4-piperidone was added. The solution was boiled in a water bath for ten minutes. From the cooled solution 1.4 g (74%) of yellow needles of a picrate, m.p. 137-138°, separated.

b) Two molecular proportions (1.0 g) of 2,5-dimethyl-4-piperidone were added to a cold solution of one molecular proportion (0.9 g) of picric acid in 5 ml of methanol, and 1.6 g (84%) of a picrate of m.p. 137-138° was isolated (yellow needles). This picrate is difficultly soluble in methanol.

	Found %:	C 47.82, 47.88;	H 5.50, 5.54;	N 15.11, 15.06
$C_{20}H_{25}O_9N_5$.	Calculated %:	C 49.68;	H 6.05;	N 14.49

The picrate of m.p. 137-138° (20 g) was decomposed with potassium carbonate, yielding 2,5-dimethyl-4-piperidone, b.p. 75-76° (n_D^{20} 1.4652; d_4^{20} 0.9767; Found MR 35.96; Calculated MR 35.96); it crystallized on cooling in beautiful nodules, m.p. 16-17°. The picrate of m.p. 137-138° (0.95 g) was dissolved in 7 ml of methanol, and one molecular proportion (0.45 g) of picric acid was added. The solution was boiled for about ten minutes. On standing, the solution yielded 0.84 g of the above-described picrate, m.p. 168-169° (rods).

* The picrates of 2,5-dimethyl-4-piperidone were investigated by G. S. Litvinenko.

The Dimethyl Ketal (IX)

2,5-Dimethyl-4-piperidone (44 g) was added carefully to a hot saturated solution of an equimolecular proportion (80 g) of picric acid in methanol. As the piperidone was added the methanol boiled gently. The picrate that precipitated from the cool solution was subjected to repeated fractional crystallization from methanol, and as a result 48 g of the above-described picrate of m.p. 168-169° was obtained together with 34 g of the picrate of the dimethyl ketal (IX), m.p. 122-123°.

	Found %:	C 43.70, 43.87;	H 5.63, 5.64;	N 14.87, 14.9
$C_{15}H_{22}O_9N_4$	Calculated %:	C 44.76;	H 5.51;	N 13.92

The picrate of m.p. 122-123° (25 g) was ground to a powder and mixed with 100 ml of 25% potassium carbonate. The mixture was shaken for two hours, and potassium picrate was filtered off and washed twice with water. The filtrate was united with the washings and saturated with potassium carbonate, and the free base was carefully extracted with ether. The ether extract was dried with potassium carbonate. Vacuum distillation yielded 9.6 g (90%) of the dimethyl ketal (IX) in the form of a colorless oil, b.p. 81-82° (6 mm); n_D^{20} 1.4595; d_4^{20} 0.9869; Found MR 47.96 Calculated MR 48.44.

	Found %:	C 61.64, 61.67;	H 10.76, 10.79;	N 7.73, 7.85
$C_9H_{19}O_2N$.	Calculated %:	C 62.43;	H 10.98;	N 8.09

Hydrolysis of the Dimethyl Ketal (IX)

The ketal (IX) of b.p. 81-82° (6 mm) (7.01 g) was heated in a water bath with 50 ml of dilute hydrochloric acid (1:1) for five hours, and 10 ml of a liquid containing methanol was then distilled off. The residue was saturated with solid caustic potash, and the piperidone that floated to the surface was extracted with ether. The ether extract was dried with potassium carbonate. Vacuum distillation yielded 4.72 g of 2,5-dimethyl-4-piperidone, b.p. 71-72° (5 mm); n_D^{20} 1.4658; d_4^{20} 0.9743, which gave a picrate, m.p. 168-169°, undepressed by an authentic sample. The 10-ml aqueous distillate, after salting out with potassium carbonate and distillation, yielded 0.68 g of methanol, b.p. 63-65°, identified by oxidation to formaldehyde in presence of hot copper gauze.

Oxidation of the α-, β-, and γ-Forms of 2,5-Dimethyl-4-piperidinol (M.p. 98°, 142°, and 87°)

The α-form of 2,5-dimethyl-4-piperidinol (m.p. 97-98°, 1.8 g) was dissolved in Beckmann's mixture (34 ml) and heated at 60° for 30 minutes. The mixture was set aside for 20 hours at room temperature, and then treated with a 50% solution of caustic potash. The base was extracted with ether, and the ether layer was dried with potassium carbonate. Vacuum distillation yielded 0.95 g of 2,5-dimethyl-4-piperidone, b.p. 70-71° (5 mm); n_D^{20} 1.4670; d_4^{20} 0.9741; Found MR 36.17; Calculated MR 35.94. Picrate: large yellow rods, m.p. 168-169°, undepressed by the corresponding picrate obtained from 2,5-dimethyl-4-piperidone.

The β- and γ-forms of 2,5-dimethyl-4-piperidinol (m.p. 142° and 87° respectively) were oxidized by the above-described procedure. The piperidones so obtained gave the same picrate of m.p. 168-169°.

SUMMARY

1. Methods have been developed for the preparation of three stereoisomers of 2,5-dimethyl-4-piperidinol (II), and numerous derivatives of these have been described.

2. By the methylation of the isomeric piperidinols (II), three stereoisomeric 1,2,5-trimethyl-4-piperidinols (VII) have been prepared, and a number of their derivatives have been described. All of the stereoisomeric benzoic esters that we have prepared (IV and VIII) have been tested for their activity as local anesthetics.

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Institute of Chemical Sciences
of the Kazakh SSR Academy of Sciences

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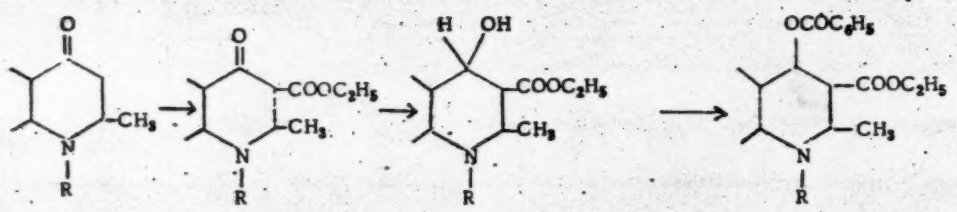
HETEROCYCLIC COMPOUNDS

COMMUNICATION XXX. CONDENSATION OF 4-PIPERIDONES WITH FORMIC, OXALIC, CARBONIC, AND CHLOROFORMIC ESTERS. SYNTHESIS OF COCAINE ANALOGS*

I. N. Nazarov, D. V. Sokolov, and G. S. Litvinenko

The various 4-piperidones that have now become readily available [1] are very important starting materials for the synthesis of new medicinals that can act as substitutes for morphine and cocaine. From 4-piperidones, Nazarov and coworkers have synthesized, in particular, the new sedative promedol, the activity of which is several times as great as that of morphine, and which has a number of other valuable advantages (low toxicity, not habit-forming, no secondary action). The local anesthetic cocaine is another important natural alkaloid, and although there are a large number of synthetic cocaine substitutes (novocaine, dicaine, etc.), the problem of finding new effective anesthetics is still of great importance. With this problem in view we decided to study the ester condensations of 4-piperidones (I) in order to obtain oxopiperidinecarboxylic esters (II) and convert them into the corresponding cocaine analogs (IV):



(I) (II) (III) (IV)

The ester condensations of 4-piperidones have received little study, there being only isolated communications on this subject in the literature [2]. A number of oxopiperidinecarboxylic esters of the type (II) have been prepared by cyclization of esters of 3,3'-iminodipropionic acids [3].

When 1,2,5-trimethyl-4-piperidone (V) was heated with diethyl carbonate in presence of sodium in absolute xylene at 95-100°, the following substances were isolated: 1,2,5-trimethyl-4-piperidinol (VI), (yield about 20%), ethyl 1,2,5-trimethyl-4-piperidyl carbonate (VII), (yield about 40%), and bis(1,2,5-trimethyl-4-piperidyl) carbonate (VIII), (yield about 15%).

Hence instead of normal ester condensation the piperidone (V) merely underwent reduction to a mixture of the stereoisomers of the piperidinol (VI), which then reacted with diethyl carbonate to give the carbonic esters (VII) and (VIII). The structures of these esters were proved by hydrolysis with 22% hydrochloric acid to the piperidinol (VI), identified by conversion to the benzoic ester (IX), which was formed also as a result of transesterification when the carbonic ester (VII) was heated with benzoyl chloride.

When the carbonic ester (VII) was hydrolyzed, not only the piperidinol (VI) was obtained, but also a small amount of the piperidone (V), which could be formed by the hydrolysis and decarboxylation of the keto ester (X), present as impurity. Reaction of the piperidone (V) with diethyl carbonate in presence of sodium ethoxide resulted in the formation of only the piperidinol (VI), it being found difficult to isolate any other products in a pure state. The same result was obtained when the piperidone (V) was heated with ethyl formate in presence of sodium methoxide:

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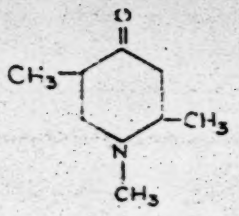

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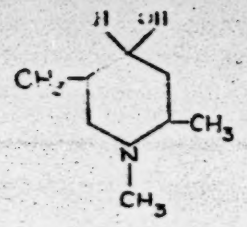

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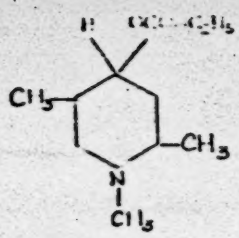

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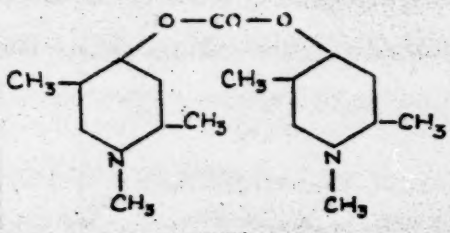
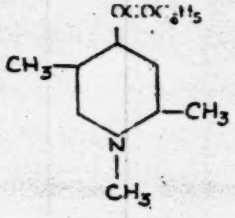


(VIII)

again only reduction to the piperidinol (VI) occurred (yield about 35%).

When the piperidone (V) was heated with sodium in absolute xylene, a white precipitate of the sodium derivative readily formed. The sodium derivative gave the original piperidone when hydrolyzed with water, and when



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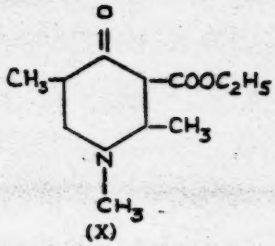
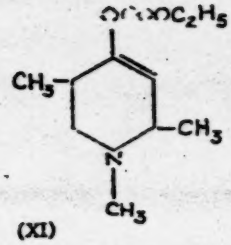
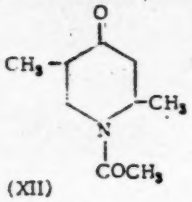


(X)

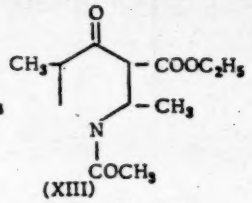


(XI)

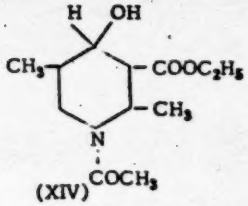
treated with ethyl chloroformate it gave the carbonic ester of the enol form (XI), (yield about 25%), which was reconverted to the piperidone (V) when hydrolyzed with hydrochloric acid. Attempts to effect the condensation of the piperidone (V) with diethyl oxalate (in presence of sodium and of sodium ethoxide) were not successful owing to resinification.



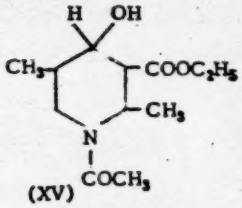
(XII)



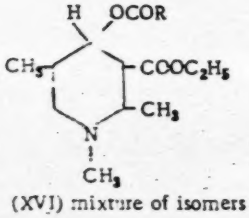
(XIII)
m.p. 65-66°



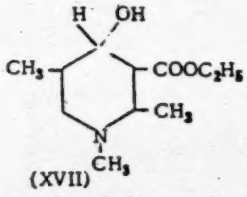
(XIV)
α) m.p. 101-102°
β) not isolated



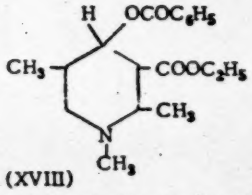
(XV)
α) m.p. 115-116°
β) m.p. 158-159°



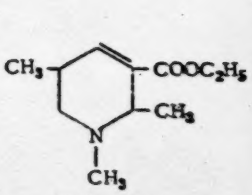
(XVI) mixture of isomers



(XVII)
α) liquid; β) m.p. 87-88°



(XVIII)
α) liquid; β) m.p. 59-60°



(XIX)

Completely different results were obtained when carbonic, formic, and oxalic esters were condensed with 1-acetyl-2,5-dimethyl-4-piperidone (XII). As in the case of alicyclic ketones, all these condensations went normally (60-70% yields), a consequence of the neutralization of the basic properties of the amine nitrogen by acetylation.

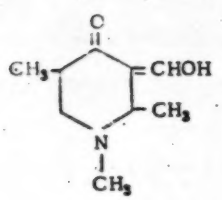
Condensation of 1-acetyl-2,5-dimethyl-4-piperidone (XII) with diethyl carbonate in presence of sodium or sodium ethoxide yielded the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII), which was hydrogenated in presence of a nickel catalyst to a mixture of stereoisomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (XIV). This last compound has four asymmetric carbon atoms, and may exist in the form of eight racemates. From the mixture of stereoisomers of the ester (XIV) we succeeded in isolating only one individual isomer, the α-isomer, m.p. 101-102°.

When the mixture of stereoisomeric acetyl esters (XIV) was heated with hydrochloric acid or with an alcoholic solution of hydrogen chloride, the acetyl group was split off, and a mixture of stereoisomers of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV) was formed, from which two individual isomers, m.p. 115-116° and 158-159°, were isolated. The low-melting α-isomer, m.p. 115-116°, was obtained also by deacetylation of the α-isomer of the acetyl nipecotic ester (XIV), m.p. 101-102°. Methylation of the individual α- and β-isomers of the piperidinol (XV) with formaldehyde and formic acid yielded the α- and β-isomers of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (XVII), which were converted by means of benzoyl chloride into the individual α- and β-isomers of the benzoic ester (XVIII).

The crystalline β-isomer of (XVII) (m.p. 87-88°) benzoylated very smoothly, whereas the liquid α-isomer of (XVII) was partially dehydrated to the unsaturated ester (XIX). The difference in the behavior of the α- and β-isomers of the piperidinol (XVII) in the benzoylation reaction is probably to be explained by a difference in the spatial disposition of their hydroxyl groups.

When the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (XIV) was benzoylated with benzoyl chloride and then deacetylated by means of hydrogen chloride, the products, obtained as mixtures of isomers, were the ethyl ester of 4-benzoyloxy-2,5-dimethylnipecotic acid (XVI, R = C_6H_5) and the corresponding acetoxy compound (XVI, R = CH_3). The latter compound was formed as a result of transfer of acetyl from nitrogen to oxygen in the course of the benzoylation reaction.

The keto ester (XIII) gave an intense red color with ferric chloride. When hydrolyzed with hydrochloric acid, it yielded 2,5-dimethyl-4-piperidone, formed by elimination of carboxyl and acetyl groups.



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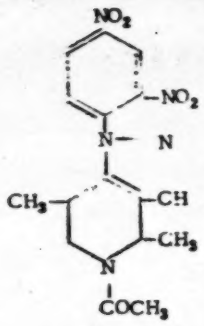
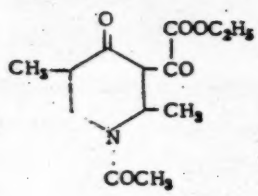
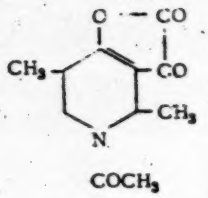


(XXI)



(XXII)



(XXIII)

When 1-acetyl-2,5-dimethyl-4-piperidone (XII) was condensed with ethyl formate in presence of sodium ethoxide in dry benzene solution, a 68% yield of the crystalline formyl derivative (XX) (shown in its hydroxymethylene enol form) was obtained; this gave an intense red color with ferric chloride, and gave the pyrazole derivative (XXI) with 2,4-dinitrophenylhydrazine. When 1-acetyl-2,5-dimethyl-4-piperidone (XII) reacted under the same conditions with diethyl oxalate, a 70% yield of the crystalline lactone (XXIII) was formed as a result of the cyclization of the oxalic ester (XXII). When the lactone (XXIII) was heated with alcohol, it was reconverted into the oxalic ester (XXII), which is an oil, but it was not found possible to isolate the latter in the pure state, for when this compound was heated, elimination of alcohol readily occurred with formation of the lactone (XXIII).

Hence, the piperidone oxalyl derivative (XXII) differs greatly in its behavior from the oxalyl derivatives of alicyclic ketones, which are considerably more stable.

EXPERIMENTAL

Sodium ethoxide was prepared by dissolving sodium in twenty times its weight of absolute alcohol. The excess of alcohol was distilled off in a bath of Wood's metal, at first at ordinary pressure, and then under somewhat reduced pressure. When a crust of sodium ethoxide began to form at the walls of the flask (which generally occurred when about two-thirds of the alcohol had been distilled off), the full vacuum of the water pump was applied. When the whole of the alcohol had been removed, the sodium ethoxide was held in a vacuum of 10-15 mm at 150-155° for a further 30 minutes, and then cooled down. The solidified alcohol-free foam of sodium ethoxide was broken up with a glass rod and then converted into a powder by energetic shaking of the closed flask. 2,5-Dimethyl-4-piperidone was prepared from 2-methyl-5-hexen-3-yn-2-ol as previously described [1]; b.p. 70-71° (5 mm); n_D^{20} 1.4670. 1-Acetyl-2,5-dimethyl-4-piperidone was prepared by the acetylation of 2,5-dimethyl-4-piperidone as described in the preceding communication [4]; b.p. 110-112° (1 mm); n_D^{20} 1.4913. 1,2,5-Trimethyl-4-piperidone was prepared from 2-methyl-5-hexen-3-yn-2-ol as described previously [1]; b.p. 71-72° (10 mm); n_D^{20} 1.4595. The nickel catalyst was prepared as follows [5]: Powdered nickel-aluminum alloy (10 g) was added in small portions over a period of 30 minutes at 50° to a vigorously stirred solution of 12.8 g of caustic soda in 50 ml of water. The mixture was maintained at this temperature for a further 50 minutes, and the alkali was then washed away with distilled water until the reaction was neutral to litmus. The catalyst was washed several times with 96% alcohol, and then with absolute alcohol.

Condensation of 1,2,5-Trimethyl-4-piperidone with Diethyl Carbonate. a) A flask containing 200 ml of absolute xylene and 9 g of sodium was heated in a water bath to melt the sodium, and the contents were then stirred while a mixture of 42 g of 1,2,5-trimethyl-4-piperidone (V) and 71 g of dry diethyl carbonate (b.p. 124-125°) was added over a period of 20 minutes. During the addition heating was discontinued, for a temperature of 96-98° was maintained by the heat of reaction. Dissolution of sodium was complete 15 minutes after the whole of the piperidone had been added, and the reaction mixture was then stirred for a further period of ten minutes at 94-96°. After removal of solvent the product was hydrolyzed with ice water (100 ml), and saturated first with carbon dioxide, and then with potassium carbonate. The base, which floated to the surface, was extracted with ether, and the ether extract was dried with sodium sulfate. Repeated vacuum fractionation yielded 8 g of 1,2,5-trimethyl-4-piperidinol (VI), b.p. 61-63° (1 mm); n_D^{20} 1.4749; d_4^{20} 0.9540, which was converted, as described in the preceding communication [4], into the benzoic ester (IX), b.p. 136-138° (1 mm); n_D^{20} 1.5170; d_4^{20} 1.031. From the isomeric mixture of benzoic esters obtained, the picrate of the β-form of the benzoic ester of 1,2,5-trimethyl-4-piperidinol, m.p. 216-218°, was isolated, and this gave no depression with an authentic sample. In this experiment, in addition to the piperidinol (VI), 6 g of bis(1,2,5-trimethyl-4-piperidyl)carbonate (VIII) was isolated as a thick yellowish oil, b.p. 129-131° (1 mm); n_D^{20} 1.4836; d_4^{20} 1.018; Found MR 87.65; Calculated MR 87.51.

Found %: N 8.72, 8.84

$C_{17}H_{32}O_3N_2$. Calculated %: N 8.97

When this ester (4.6 g) was hydrolyzed with 22% hydrochloric acid (100 ml) for 15 hours in a boiling water bath, the product was 1,2,5-trimethyl-4-piperidinol (2.1 g) b.p. 61-62° (1 mm); n_D^{20} 1.4756; d_4^{20} 0.9547

Found %: N 10.14

$C_8H_{17}ON$. Calculated %: N 9.79

The picrate of the dipiperidyl carbonate (VIII) melted at 215-216° (from methanol).

Found %: N 12.64, 12.82

$C_{13}H_{25}O_{16}N_5$. Calculated %: N 19.94

In this experiment also 10 g of intermediate fractions and 9 g of resin were obtained.

b) 1,2,5-Trimethyl-4-piperidone (17.6 g) was added to 2.3 g of sodium melted under 80 ml of absolute xylene. The mixture was heated for 30 minutes at 100° (until all of the sodium had dissolved), and diethyl carbonate (24 g) was then added and heating was discontinued. After 30 minutes the mixture was cooled and acidified with hydrochloric acid (1:1). The aqueous layer was saturated with potassium carbonate, and the base was extracted with ether. The ether layer was dried with sodium sulfate, and the ether was driven off, leaving 22 g of a dark-red oil. The whole reaction was repeated three times, and the united crude product (86 g) was repeatedly fractionated under reduced pressure, yielding 3 g of 1,2,5-trimethyl-4-piperidinol (VI) b.p. 62-63° (1 mm); n_D^{20} 1.4751; d_4^{20} 0.9562; 10 g of the above-described bis(1,2,5-trimethyl-4-piperidyl) carbonate (VIII), b.p. 129-131° (1 mm); n_D^{20} 1.4840; d_4^{20} 1.019; which gave 1,2,5-trimethyl-4-piperidinol when hydrolyzed with hydrochloric acid; and 33 g of

ethyl 1,2,5-trimethyl-4-piperidyl carbonate (VII) as a colorless mobile liquid, b.p. 82-84° (1 mm); n_D^{20} 1.4547; d_4^{20} 1.1005; found MR 57.99; calculated MR 58.02.

	Found %:	N 6.88; 6.94
$C_{11}H_{21}O_2N$.	Calculated %:	N 6.51

When this ester was heated with benzoyl chloride (two hours at 165-170°), transesterification occurred with formation of the benzoic ester of 1,2,5-trimethyl-4-piperidinol (IX), b.p. 137-139° (1 mm); n_D^{20} 1.5145; d_4^{20} 1.041, identified by isolation of the picrate of the β-form, m.p. 216-216°, and by a mixture melting-point test with an authentic sample.

Hydrolysis of the ester VII with 22% hydrochloric acid at the boil yielded 1,2,5-trimethyl-4-piperidinol, b.p. 91-93° (5 mm); n_D^{20} 1.4748, and a very small amount of 1,2,5-trimethyl-4-piperidinol (V), identified by preparation of the picrate, m.p. 168-169°, and by a mixture melting-point test with an authentic sample.

c) Absolute xylene (100 ml) was added to dry sodium ethoxide powder prepared from 9.2 g of sodium, the temperature of the mixture was raised to 90°, and 1,2,5-trimethyl-4-piperidone (28.6 g) was added. The mixture was stirred for ten minutes, and dry diethyl carbonate (47 g) was added. After 15 minutes, xylene was removed from the yellowish reaction mixture under reduced pressure; the residue was decomposed with ice (80 g), and then saturated first with carbon dioxide and then with potassium carbonate. The red oil that floated on the surface was dried with sodium sulfate and vacuum-fractionated three times, yielding 6.3 of 1,2,5-trimethyl-4-piperidinol, b.p. 59-60° (0.8 mm); n_D^{20} 1.4750; d_4^{20} 0.9566.

	Found %:	N 9.92; 9.76
$C_8H_{17}ON$.	Calculated %:	N 9.79

In this experiment, apart from the piperidinol VI, 6 g of higher fractions and 9.4 g of resin were obtained.

d) The condensation with sodium ethoxide was carried out also at room temperature (standing for three days), and 14 g of 1,2,5-trimethyl-4-piperidone, 24 g of diethyl carbonate, and 27 g of dry sodium ethoxide (9.2 g of sodium) yielded 5.2 g of 1,2,5-trimethyl-4-piperidinol (VI), b.p. 99-101° (9 mm); n_D^{20} 1.4748, and 4.5 g of resin. The piperidinol VI was identified by conversion into its benzoic ester (IX) and by isolation of the picrate of the β-form (m.p. 216-218°, undepressed by authentic sample).

Preparation of the Sodium Derivative of 1,2,5-Trimethyl-4-piperidone, and Its Hydrolysis. Sodium (2.3 g) was melted under 50 ml of absolute toluene, the mixture was vigorously stirred, and 1,2,5-trimethyl-4-piperidone (14 g), dissolved in 20 ml of absolute toluene, was added at 97-100° over a period of one hour. Dissolution of the sodium was complete ten minutes after addition of the whole of the piperidone. The white precipitate of the sodium derivative of 1,2,5-trimethyl-4-piperidone that had formed was hydrolyzed with water (30 ml). The aqueous layer was saturated with potassium carbonate, and the product was extracted with toluene, dried with potassium carbonate, and vacuum-fractionated, yielding 9.6 g of the starting material, 1,2,5-trimethyl-4-piperidone (V), b.p. 88-89° (20 mm); n_D^{20} 1.4587; its picrate melted at 168-169°, and gave no depression with the picrate of the original piperidone.

Condensation of 1,2,5-Trimethyl-4-piperidone with Ethyl Formate. A solution of 32 g of dry ethyl formate (b.p. 54-55°) and 28 g of 1,2,5-trimethyl-4-piperidone in 30 ml of absolute benzene was added to a boiling suspension of dry sodium methoxide (from 9.2 g of sodium) in 100 ml of absolute benzene. The mixture was boiled for two hours, and the solvent was distilled off under reduced pressure. The brown residue was dissolved in 75 ml of 15% hydrochloric acid, and the solution was saturated with potassium carbonate. The product was extracted with ether, the ether extract was dried with sodium sulfate, and the ether was driven off. Vacuum fractionation yielded 9 g of 1,2,5-trimethyl-4-piperidinol (VI), b.p. 49-51° (0.5 mm); n_D^{20} 1.4749; d_4^{20} 0.9540; found MR 40.29; calculated MR 40.42.

	Found %:	N 10.19; 10.04
$C_8H_{17}ON$.	Calculated %:	N 9.79

The 1,2,5-trimethyl-4-piperidinol (VI) obtained was identified by its conversion into the benzoic ester (IX), b.p. 120-121° (0.5 mm); n_D^{20} 1.5180; d_4^{20} 1.031, and by the isolation from this mixture of stereoisomeric benzoic esters of the picrate of the β-form, m.p. 216-218°, undepressed by an authentic sample. In this experiment, apart from the piperidinol VI, 8.5 g of intermediate fractions and 4.5 g of resin were obtained. When the condensation was carried out in the cold, the piperidinol VI was not formed: the reaction product was a red oil, which did not crystallize and could not be distilled without decomposition at 1 mm. The oil gave an intense red color with ferric chloride.

Condensation of 1,2,5-Trimethyl-4-piperidinol with Ethyl Chloroformate. A solution of 11 g of freshly distilled ethyl chloroformate in 10 ml of dry toluene was added dropwise to a vigorously stirred, cooled (10-12°) suspension of the sodium derivative of 1,2,5-trimethyl-4-piperidone, prepared as described above from 14 g of the piperidone and 2.3 g of sodium. After 30 minutes, the sodium chloride that had formed was washed out with water, and the product was extracted with toluene. The extract was dried with sodium sulfate, the toluene was distilled off, and the residue was vacuum-fractionated three times, yielding 6.3 g of ethyl 1,2,5,6-tetrahydro-1,2,5-trimethyl-4-pyridyl carbonate (XI) as a colorless mobile liquid, b.p. 73-76° (1 mm); n_D^{20} 1.4640; d_4^{20} 1.019; found MR 57.67; calculated MR 57.55.

	Found %:	N 6.85; 6.78
$C_{11}H_{19}O_2N$.	Calculated %:	N 6.57

There were also obtained 1 g of the original 1,2,5-trimethyl-4-piperidone (identified by the picrate), 5 g of intermediate fractions, and 2 g of tar. The picrate of the ester XI melted at 143-144° (from methanol).

	Found %:	N 12.90; 12.84
$C_{17}H_{22}O_{10}N_4$.	Calculated %:	N 12.67

The ester XI (5.3 g) and 100 ml of 22% hydrochloric acid were heated in a boiling water bath for ten hours. The usual treatment yielded 1.6 g of 1,2,5-trimethyl-4-piperidone (V), b.p. 64-65° (5 mm); n_D^{20} 1.4590, which gave a picrate of m.p. 168.5-169°, undepressed by an authentic sample.

Condensation of 1-Acetyl-2,5-dimethyl-4-piperidone with Diethyl Carbonate. a) In a flask fitted with mechanical stirrer and reflux condenser protected with a calcium chloride tube, a mixture of 25.4 g (0.15 mole) of 1-acetyl-2,5-dimethyl-4-piperidone (XII), 35.4 g (0.3 mole) of diethyl carbonate (b.p. 125-126°; dried over sodium), and 4.5 g of sodium was heated until the sodium melted (100°). Exothermic reaction accompanied by frothing set in. After 30 minutes the reaction mixture was cooled, hydrolyzed with water (about 30 ml), and acidified with hydrochloric acid. The product was extracted with benzene, and the extract was dried with sodium sulfate. After removal of solvent, two vacuum fractionations yielded 12 g (33%) of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII) as a thick colorless oil, b.p. 136-138° (1.5 mm); n_D^{20} 1.4975; d_4^{20} 1.1245; found MR 62.75; calculated MR for the keto form 61.04, and for the enol form 62.08.

	Found %:	N 5.67; 5.98
$C_{12}H_{19}O_4N$.	Calculated %:	N 5.81

The condensation product gave an intense red color with an alcoholic solution of ferric chloride. During the condensation much resinification occurred: 13.9 g of resin remained after the fractionations. When a lower excess (20%) of diethyl carbonate was used, the yield was reduced to 16%.

b) A mixture of 25.4 g of 1-acetyl-2,5-dimethyl-4-piperidone, 35.4 g of diethyl carbonate, and sodium ethoxide powder obtained from 6.9 g of sodium was stirred at 90° for 40 minutes. The product was hydrolyzed with water (40 ml), acidified with concentrated hydrochloric acid, saturated with common salt, extracted with benzene, dried with sodium sulfate, and vacuum-fractionated, yielding 13.2 g (36.5%) of the above-described ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII), b.p. 141-142° (1.7 mm); n_D^{20} 1.4982; d_4^{20} 1.1243.

	Found %:	N 6.29; 6.23
$C_{12}H_{19}O_4N$.	Calculated %:	N 5.81

A residue of 11.2 g of resin remained in the flask. When the condensation temperature was reduced, the yield was progressively improved: 42% at 80°, and 54% at room temperature (15-20°). When a lower excess (30%) of diethyl carbonate was used, the yield obtained at room temperature was reduced to 46%. The best yield (55%) was obtained when the condensation was carried out as described below.

c) A mixture of 25.4 g of 1-acetyl-2,5-dimethyl-4-piperidone, 35.4 g of dry diethyl carbonate, and sodium ethoxide powder prepared from 4.6 g of sodium was kept in a closed flask at 15-20° for ten days. The product was treated as described above, and yielded 20 g (55%) of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII), b.p. 134-136° (1 mm); n_D^{20} 1.4938. After long standing the product crystallized, and it was recrystallized from petroleum ether in the form of needles, which formed rodlike clusters, m.p. 65-66°.

	Found %:	N 6.07; 5.77
$C_{12}H_{19}O_4N$.	Calculated %:	N 5.81

Hydrolysis of the Ethyl Ester of 1-Acetyl-2,5-dimethyl-4-oxonipecotic Acid. A mixture of 8.1 g of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (b.p. 134-136°/1 mm) and 100 ml of 22% hydrochloric acid was heated in a boiling water bath for 32 hours. The hydrochloric acid was distilled off under reduced pressure,

and the residue was dissolved in water. The aqueous solution was saturated with potassium carbonate, and the base was extracted with ether, dried with potassium carbonate, and vacuum-distilled, yielding 2.5 g of 2,5-dimethyl-4-piperidone, b.p. 72-73° (6 mm); n_D^{28} 1.4670. Its picrate melted at 168-169° and gave no depression with the picrate of authentic 2,5-dimethyl-4-piperidone.

Hydrogenation of the Ethyl Ester of 1-Acetyl-2,5-dimethyl-4-oxonipecotic Acid. Nickel catalyst (about 5 g) was added to a solution of 16 g of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (b.p. 134-136°/1 mm) in 80 ml of absolute alcohol. In the course of 14 hours' shaking, 1.65 liter of hydrogen was absorbed, against 1.66 liter required by theory. The solution gave no color with ferric chloride. After filtration from catalyst and removal of alcohol, the hydrogenation product was vacuum-fractionated, yielding

Fraction I, b.p. 151-156° (1 mm), 2.5 g
Fraction II, b.p. 156-161° (1 mm), 5.7 g
Fraction III, b.p. 161-170° (1 mm), 5.9 g

All three fractions were mixtures of stereoisomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (XIV).

Fraction I, b.p. 151-156° (1 mm): n_D^{20} 1.4402; d_D^{20} 1.105; found MR 63.58; calculated MR 62.55.

Found %: N 6.00; 6.06
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

Fraction II, b.p. 156-161° (1 mm); n_D^{20} 1.4902; d_4^{20} 1.1185; found MR 62.85; calculated MR 62.55.

Found %: N 5.90
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

After standing for a long time, this fraction partially crystallized. The crystals were separated and recrystallized from petroleum ether, yielding 1.6 g of an isomer of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid having m.p. 101-102°.

Found %: N 5.80; 5.92
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

Fraction III, b.p. 161-170° (1 mm); n_D^{20} 1.4892; d_4^{20} 1.125; found MR 62.38; calculated MR 62.55.

Found %: N 5.57; 5.95
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

Ethyl Ester of 4-Hydroxy-2,5-dimethylnipecotic Acid. a) A mixture of isomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid obtained as described above by the hydrogenation of 14.6 g of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII) in presence of a nickel catalyst was dissolved in 150 ml of absolute alcohol. The solution was saturated with dry hydrogen chloride and boiled under reflux for 28 hours. The solvent was distilled off, and the residue was vacuum-dried and again dissolved in 150 ml of absolute alcohol, saturated with hydrogen chloride, and boiled under reflux for 10 hours. The alcohol was driven off, and the residue of hydrochloride was dissolved in water (30 ml), washed with benzene, decomposed with potassium carbonate, and extracted with ether. During extraction a precipitate formed of the ether-insoluble high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), which was recrystallized from dry benzene, yielding 3.4 g of leaves, m.p. 158-159°.

Found %: N 7.10; 7.28
$C_{10}H_{19}O_3N$. Calculated %: N 6.92

Found: M 200.5; 200.4; (titration with 0.1 N HCl with methyl orange indicator)
Calculated: M 201.3

Picrate: yellow hexagonal plates, m.p. 204-205° (from absolute alcohol):

Found %: C 45.07; 44.93; H 5.18; 5.24; N 12.60; 12.52
$C_{16}H_{22}O_{10}N_4$. Calculated %: C 44.65 H 5.15 N 13.03

Hydrochloride: colorless scales, m.p. 198-199° (reprecipitation from alcohol with ether).

The ether extract obtained after separation of crystals of m.p. 158-159° was dried with sodium sulfate, and the solvent was then distilled off. When the oil that remained was vacuum-distilled, it boiled over a wide range (103-180°/1.5 mm), and it was, therefore, again boiled with an anhydrous alcoholic solution of hydrogen chloride (twice: 36 and

17 hours). To the oil obtained after the usual treatment (3.7 g), three times its amount of dry ether was added. The crystals that came down after a while (2.1 g) were recrystallized from dry benzene, and yielded 1.2 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), which formed clusters of needles, m.p. 115-116°.

Found %: N 7.14; 6.77
$C_{10}H_{19}O_3N$. Calculated %: N 6.92

Found: M 200.3; 200.1
Calculated: M 201.3

The product was generally of good solubility in organic solvents, but did not dissolve readily in petroleum ether. It was difficult to recrystallize owing to its tendency to form supersaturated solutions.

Picrate: nodules, m.p. 142-143° (from a mixture of alcohol and petroleum ether).

Found %: N 12.75; 12.84
$C_{16}H_{22}O_{10}N_4$. Calculated %: N 13.03

Hydrochloride: fine crystals, m.p. 185-186° (reprecipitated from alcohol with ether).

In this experiment there was isolated also 2 g of the original ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid, b.p. 145-163° (1 mm); n_D^{20} 1.4802; d_4^{20} 1.118.

b) A solution of 16.2 g of a mixture of isomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid, obtained by hydrogenation of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid in presence of a nickel catalyst, in 400 ml of 10% hydrochloric acid was heated in a water bath for 60 hours. The hydrolysis product, after complete removal of hydrochloric acid under reduced pressure, was dissolved in 150 ml of absolute alcohol, and the solution was boiled in presence of hydrogen chloride for 16 hours in order to esterify the carboxyl group. The alcohol was distilled off, the residue was treated with potassium carbonate, and the base was extracted with ether. The substance that was then precipitated was separated and recrystallized from dry benzene, yielding 3.2 g of the ether-insoluble high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), m.p. 158-159°. After removal of ether from the ether extract and crystallization of the residue from dry benzene, 2.3 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV) of m.p. 115-116° was obtained.

c) A solution of 1.4 g of the crystalline isomer of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (m.p. 101-102°) in 100 ml of absolute alcohol was saturated with dry hydrogen chloride and boiled under reflux for 30 hours. The usual treatment yielded 0.6 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), m.p. 115-116°, and 0.6 g of the original substance, m.p. 101-102°, was recovered unchanged.

When the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (16.5 g) was reduced with 2.5% sodium amalgam (750 g) in 45% aqueous alcohol (150 ml), and the product was heated with hydrogen chloride in absolute alcohol to eliminate the acetyl group, the products were 1.4 g of the high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid, m.p. 158-159°, and 5 g of a mixture of isomers, b.p. 103-122°/1.5 mm, from which 0.8 g of the low-melting α-isomer, m.p. 115-116°, was isolated.

Ethyl Esters of 4-Acetoxy- and 4-Benzoyloxy-2,5-dimethylnipecotic Acids. Freshly distilled benzoyl chloride (10 g) was heated with 14.3 g of the mixture of isomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid obtained by hydrogenation of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid in presence of a nickel catalyst; the temperature was 170°, and heating was continued until evolution of hydrogen chloride ceased (15 minutes). A current of dry hydrogen chloride was then passed through the reaction mixture for one hour at 160°. The product was dissolved in water, washed with benzene, and treated with potassium carbonate. The base was extracted with benzene, dried with sodium sulfate, and vacuum-fractionated, yielding 1.5 g of the ethyl ester of 4-acetoxy-2,5-dimethylnipecotic acid (XVI, R = CH_3), b.p. 101-102° (1 mm); n_D^{20} 1.4610; d_4^{20} 1.065; found MR 62.82; calculated MR 62.32.

Found %: N 6.18; 6.14
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

The fractionation yielded also 0.9 g of the ethyl ester of 4-benzoyloxy-2,5-dimethylnipecotic acid (XVI, R = C_6H_5), b.p. 160-164° (1 mm); n_D^{20} 1.5123; d_4^{20} 1.1145; found MR 82.16; calculated MR 81.81.

Found %: N 4.97; 4.90.
$C_{17}H_{23}O_4N$. Calculated %: N 4.59

Each of these esters is a mixture of stereoisomers, and they give oily picrates and hydrochlorides.

Ethyl Ester of 4-Hydroxy-1,2,5-trimethylnipecotic Acid (XVII, α-isomer). A mixture of 4.4 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (m.p. 115-116°), 3.4 g of 29% formaldehyde, and 1.4 g of 90% formic acid was heated in a boiling water bath until carbon dioxide ceased to be evolved (40 minutes). The cooled solution was treated with potassium carbonate, and the base was extracted with ether, dried with magnesium sulfate, and vacuum-distilled, yielding 4.3 g of the α-isomer of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (XVII), b.p. 112-113° (1 mm); n_D^{25} 1.4778; d_1^{25} 1.0528; found MR 57.86; calculated MR 57.93.

	Found %:	C 62.02; 61.98; H 9.99; 10.04; N 6.58; 6.52
$C_{11}H_{21}O_3N$.	Calculated %:	C 61.36; H 9.83 N 6.51

Found: M 215.4; 214.5 (titration)
Calculated: M 215

Picrate: yellow rods, m.p. 141-142° (from absolute alcohol).

	Found %:	N 12.83; 12.31
$C_{17}H_{24}O_{10}N_4$.	Calculated %:	N 12.61

Hydrochloride: colorless rosettes, m.p. 151-152° (reprecipitated from alcohol with ether).

Ethyl Esters of 4-Benzoyloxy-1,2,5-trimethylnipecotic Acid (XVIII, α-isomer) and of 1,2,5,6-Tetrahydro-1,2,5-trimethylnicotinic Acid (XIX). A mixture of 3.6 g of the above-described hydrochloride of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (m.p. 151-152°) and 6.1 g of freshly distilled benzoyl chloride was heated at 160° until evolution of hydrogen chloride ceased (30 minutes). The excess of benzoyl chloride was distilled off under reduced pressure, and the residue was dissolved in water, washed with ether, and treated with potassium carbonate. The base was extracted with ether, dried with magnesium sulfate, and vacuum-fractionated, yielding 0.7 g of the ethyl ester of 1,2,5,6-tetrahydro-1,2,5-trimethylnicotinic acid (XIX) as a slightly yellowish, mobile oil, b.p. 109-110° (8 mm); n_D^{20} 1.4765; d_4^{20} 0.9940; found MR 56.02; calculated MR 55.94.

	Found %:	N 7.15; 7.16
$C_{11}H_{19}O_2N$.	Calculated %:	N 7.10

Found: M 201.4; 202.3 (titration)
Calculated: M 197.3

Picrate: noncrystallizing oil. Hydrochloride: colorless clusters, m.p. 137-138° (precipitation from alcohol with ether). The fractionation yieldedalso 2 g of the ethyl ester of 4-benzoyloxy-1,2,5-trimethylnipecotic acid (XVIII, α-isomer) as a greenish oil, b.p. 167-170° (2 mm); n_D^{22} 1.5205; d_4^{20} 1.0872; found MR 87.97; calculated MR 86.78.

	Found %:	N 4.78; 4.55
$C_{18}H_{25}O_4N$.	Calculated %:	N 4.39

Picrate: yellow plates, m.p. 184-185° (from absolute alcohol).

	Found %:	N 10.34; 9.97
$C_{24}H_{28}O_{11}N_4$.	Calculated %:	N 10.22

Hydrochloride: fine colorless leaves, m.p. 185-186° (precipitation from alcohol with ether).

Ethyl Ester of 4-Hydroxy-1,2,5-trimethylnipecotic Acid (β-isomer). The high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (m.p. 158-159°; 4.1 g) was methylated with formaldehyde and formic acid as described above. Removal of ether, followed by recrystallization of the residue from gasoline (b.p. 80-90°), yielded 3.8 g (88%) of the β-isomer of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (XVII), m.p. 87-88°.

	Found %:	C 61.72; 61.77; H 9.96; 10.05; N 6.53; 6.49
$C_{11}H_{21}O_3N$.	Calculated %:	C 61.36; H 9.83; N 6.51

Found: M 215.2; 215.1 (titration)
Calculated: M 215

Picrate: yellow needles, m.p. 168-169° (from absolute alcohol).

	Found %:	N 12.46; 12.51
$C_{17}H_{24}O_{10}N_4$.	Calculated %:	N 12.61

Hydrochloride: colorless leaves, m.p. 174-175° (reprecipitation from alcohol with ether).

Ethyl Ester of 4-Benzoyloxy-1,2,5-trimethylnipecotic Acid (β-isomer). A mixture of 3.7 g of the hydrochloride of the β-isomer of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (m.p. 174-175°) and 6.3 g of freshly distilled benzoyl chloride was heated at 160° until the evolution of hydrogen chloride ceased (30 minutes). The excess of benzoyl chloride was distilled off under reduced pressure, and the residue was mixed with water (about 15 ml). The crystals that came down were pressed off at the pump and reprecipitated from alcohol with ether, yielding 2.5 g of the hydrochloride of the ethyl ester of 4-benzoyloxy-1,2,5-trimethylnipecotic acid (β-isomer) in the form of leaves of m.p. 213-214°. The aqueous solution remaining after removal of the crystals of hydrochloride was washed with ether and treated with potassium carbonate. The base was extracted with ether and, after being dried with magnesium sulfate, was vacuum-distilled, yielding 1.9 g of the ethyl ester of 4-benzoyloxy-1,2,5-trimethylnipecotic acid (XVIII, β-isomer), b.p. 167-169° (2 mm); n_D^{25} 1.5103; d_4^{25} 1.088; found MR 87.75; calculated MR 86.76. When the amount of hydrochloride isolated was taken into account, the total yield of this benzoic ester was 90%. On standing, the free base crystallized, and recrystallization from petroleum ether yielded rhombic plates, m.p. 59-60°.

	Found %:	C 67.71; 67.86;	H 8.01; 7.99;	N 4.27; 4.38
$C_{18}H_{25}O_4N$.	Calculated %:	C 67.68;	H 7.89;	N 4.39

The hydrochloride of this ester melted at 213-214° (precipitated from alcohol with ether) and gave no depression with the above-described hydrochloride, which was directly isolated from the benzoylation products.

Condensation of 1-Acetyl-2,5-dimethyl-4-piperidone with Ethyl Formate. Ethylformate (b.p. 53-54°) (7.1 g) and a solution of 8.1 g of 1-acetyl-2,5-dimethyl-4-piperidone in 150 ml of absolute benzene were added, with continuous stirring and cooling with ice water, to dry sodium ethoxide prepared from 2.2 g of sodium. The mixture was set aside for 40 hours in a hermetically closed flask, and the precipitate that had formed was then filtered off, washed with benzene, and dissolved in presence of small pieces of ice in concentrated hydrochloric acid (20 ml). The solution was saturated with common salt, and the condensation product was extracted with benzene. The extract was dried with sodium sulfate, and, after removal of the greater part of the solvent, the solid present was recrystallized from benzene, yielding 6.5 g (68%) of crystalline 3-hydroxymethylene-1,2,5-trimethyl-4-piperidone (XX), m.p. 123-124°.

	Found %:	N 7.24; 7.29
$C_{10}H_{15}O_3N$.	Calculated %:	N 7.11

In other condensation experiments, the product was vacuum-distilled, and a thick colorless oil, b.p. 138-139°/1 mm, was obtained, which solidified when cold to crystals of m.p. 123-124°. The condensation product (XX) gave an intense red color with ferric chloride. When treated with an alcoholic solution of 2,4-dinitrophenylhydrazine acidified with hydrochloric acid, the condensation product yielded a pyrazole derivative (XXI), m.p. 201-202°.

	Found %:	N 19.66; 19.75
$C_{16}H_{17}O_5N_5$.	Calculated %:	N 19.50

When the formyl derivative XX was hydrogenated in presence of a nickel catalyst, two molecular proportions of hydrogen were absorbed. When the condensation was performed at 80° (at the boil in benzene), the yield of hydroxymethylene derivative (XX) remained practically unchanged. The order in which the piperidone and ethyl formate were added to the sodium ethoxide also had no effect on the yield.

Condensation of 1-Acetyl-2,5-dimethyl-4-piperidone with Diethyl Oxalate. Diethyl oxalate (b.p. 90-91°/15 mm) (29 g) and a solution of 17 g of 1-acetyl-2,5-dimethyl-4-piperidone in 30 ml of absolute benzene were added, with continuous stirring and cooling with ice water, to a suspension of dry sodium ethoxide (obtained from 4.2 g of sodium) in 100 ml of absolute benzene. The reaction mixture was set aside at room temperature overnight, and was then acidified, under cooling, with hydrochloric acid. The condensation product was extracted with benzene, and the white powder that then formed was filtered off, yielding 3.3 g of the lactone XXIII, m.p. 210° (with frothing). The oil remaining after removal of benzene (this oil gave a red color with ferric chloride) was heated for 15 minutes at 150-160°, after which a further 12.2 g of the lactone XXIII was isolated in the form of a white powder, m.p. 211° (with frothing). The total yield of lactone was 15.5 g (68%).

	Found %:	C 59.24; 59.08;	H 5.89; 6.15;	N 6.29; 6.24
$C_{11}H_{15}O_4N$.	Calculated %:	C 59.19;	H 5.83;	N 6.28

The lactone was found to have very low solubility in the usual organic solvents and in water. It was readily soluble in alkalis, and was reprecipitated by acid. It gave a green color with an alcoholic solution of ferric chloride.

When boiled with alcohol it was converted into the original oily substance, which gave a red color with ferric chloride, and was probably 1-acetyl-2,5-dimethyl-4-oxo-3-piperidyl ethyl oxalate (XXII). When this condensation was carried out with an alcoholic solution of sodium ethoxide and with sodium in benzene, analogous results were obtained.

SUMMARY

1. The condensations of 1,2,5-trimethyl-4-piperidone and of 1-acetyl-2,5-dimethyl-4-piperidone with diethyl carbonate, with diethyl oxalate, and with ethyl formate have been investigated.

2. It has been shown that in these condensations, 1,2,5-trimethyl-4-piperidone is reduced by the sodium or sodium ethoxide present to 1,2,5-trimethyl-4-piperidinol, whereas 1-acetyl-2,5-dimethyl-4-piperidone gives the normal condensation products in 60-70% yield.

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EXCHANGE OF HYDROGEN ATOMS OF SATURATED CYCLIC HYDROCARBONS WITH SULFURIC ACID

V. N. Setkina, D. N. Kursanov, and A. L. Liberman

In a previous communication [1] we have described the results of an investigation of the exchange reactivity of the hydrogen atoms of saturated aliphatic hydrocarbons when treated with heavy (deuterium-rich) sulfuric acid. By means of tracer technique we showed that saturated aliphatic hydrocarbons containing tertiary carbon atoms underwent hydrogen exchange in presence of heavy sulfuric acid. On the other hand, saturated aliphatic hydrocarbons in which there were no tertiary carbon atoms did not undergo hydrogen exchange with sulfuric acid.

In the present paper we describe results of an investigation of the exchange reactivity of hydrogen atoms in saturated cyclic hydrocarbons of various structure when treated with heavy sulfuric acid. The constants of the original hydrocarbons are given in Table 1.

TABLE 1

Expt. No.	Hydrocarbon	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
1	Cyclohexane	80.4-80.5 (760)	1.4263	0.7782
2	Methylcyclohexane	100.3-100.4 (755)	1.4230	0.7696
3	1,1-Dimethylcyclohexane	119.9 (760)	1.4294	0.7810
4	1-Ethyl-4-methylcyclohexane (mixture of cis and trans isomers)	149.3-152.2 (760)	1.4326	0.7851
5	1,4-Dimethylcyclohexane (trans isomer)	119.5 (761)	1.4209	0.7627
6	Cyclopentane	49.0 (760)	1.4065	0.7452
7	Methylcyclopentane	71.8 (760)	1.4098	0.7485
8	Decahydronaphthalene (trans isomer)	72.0-72.5 (18)	1.4692	0.8690
9	Decahydronaphthalene (30% cis + 70% trans)	59.6-62.0 (10)	1.4739	–

Treatment with heavy sulfuric acid (monohydrate, or acid containing traces of SO_3) was carried out at 20-25° in sealed tubes, which were placed in a shaker (160-180 shakes per minute). After the experiment the hydrocarbons were purified as in the case of the acyclic hydrocarbons [1], and were then subjected to combustion over red-hot copper oxide. The water obtained was suitably purified, and the amount of deuterium in the hydrocarbon under investigation was determined from the density excess of this combustion water. Results for hydrogen exchange in hydrocarbons of the cyclohexane series are given in Table 2, and results for cyclopentane hydrocarbons are given in Table 3.

TABLE 2

Expt. No.	Hydrocarbon	Amount (moles)		Duration of reaction (hr)	Excess density of combustion water (γ)			Exchange (% of value calcd. for exchange of all H)
		of acid	of h.c.		calculated* for 1 H	calculated* for all H	found	
1	Cyclohexane	0.050	0.033	3	–	19350	272	1.4
2	Methylcyclohexane	0.054	0.027	3	5532	21418	20915	98
3	Methylcyclohexane	0.058	0.029	10.5	5525	21290	20650	97
4	Methylcyclohexane	0.053	0.022	26	5748	25060	24890	99
5	1,4-Dimethylcyclohexane (trans)	0.040	0.020	12	–	3228	3214	99
6	1-Ethyl-4-methylcyclohexane (mixture of cis and trans)	0.058	0.019	11	–	24235	20100	83
7	1-Ethyl-4-methylcyclohexane (mixture of cis and trans)	0.055	0.012	25	–	5390	5176	96
8	1,1-Dimethylcyclohexane	0.051	0.016	4	–	5000	89	1.8

* In the calculations, the distribution coefficient is taken to be unity.

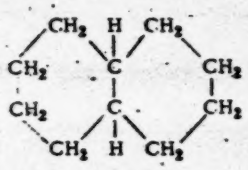
TABLE 3

Expt. No.	Hydrocarbon	Amount (moles) of acid	Amount (moles) of h.c.	Duration of reaction (hr)	Excess density of combustion water (γ) calculated for 1 H	calculated for all H	found	Exchange (% of value calcd. for exchange of all H)
1	Cyclopentane	0.059	0.054	1	–	2980	56	1.9
2	Cyclopentane	0.042	0.022	3	–	4193	98	2.3
3	Cyclopentane	0.045	0.028	50	–	3719	94	2.5
4	Methylcyclopentane	0.021	0.035	1	188	378	202	54
5	Methylcyclopentane	0.060	0.030	1	1116	4014	2118	53
6	Methylcyclopentane	0.046	0.046	2.5	940	2399	1578	66
7	Methylcyclopentane	0.047	0.027	3	984	3362	2526	75
8	Methylcyclopentane	0.041	0.027	4	970	3117	2590	83
9	Methylcyclopentane	0.060	0.033	5	972	3386	2926	90
10	Methylcyclopentane	0.048	0.018	10	1071	4507	4214	94
11	Methylcyclopentane	0.063	0.020	15	1104	5276	5068	96
12	Methylcyclopentane	0.062	0.024	14	1119	4848	4807	99

The results given in Tables 2 and 3 show that the presence in a cycloalkane ring of tertiary carbon atoms greatly influences the reactivity of the whole molecule. Thus, in a cyclohexane ring containing a tertiary carbon atom all the hydrogen atoms become reactive and exchange equilibrium is established at room temperature in several hours (Expt. No. 2, 3, 4, and 5, Table 2), whereas cyclohexane and 1,1-dimethylcyclohexane do not undergo hydrogen exchange (Expt. No. 1 and 8, Table 2).

The cyclopentane hydrocarbons present a similar picture: methylcyclopentane undergoes hydrogen exchange, equilibrium being established in 14-15 hours (Expt. No. 11 and 12, Table 3), whereas cyclopentane shows no appreciable tendency to enter into this reaction (Expt. No. 1, 2, and 3, Table 3).

Investigation of the tendency of trans-decahydronaphthalene (I)



(I)

and a mixture of cis- and trans-decahydronaphthalene to undergo hydrogen exchange led us, however, to unexpected results. On the basis of the results cited above (Tables 2 and 3) it might be expected that the presence in the decahydronaphthalene molecule of two tertiary carbon atoms would make this compound prone to hydrogen exchange in presence of sulfuric acid. It was found, however, that neither of the isomers of decahydronaphthalene underwent hydrogen exchange, even after long contact with sulfuric acid (Table 4). It will be noted that the tertiary carbons of decahydronaphthalene, unlike those in the previously studied compounds, are concerned in bridge formation. The question of exchange reactivity at such carbons is in need of further investigation.

Our investigation has, therefore, shown that the rule determining the tendency for saturated hydrocarbons to undergo hydrogen exchange is general both for aliphatic and cyclic hydrocarbons; as indicated, the only exception is decahydronaphthalene.

TABLE 4

Expt. No.	Hydrocarbon	Amount (moles) of acid	Amount (moles) of h.c.	Duration of reaction (hr)	Excess density of combustion water (γ) calculated for 1 H	calculated for all H	found	Exchange (% of value calcd. for exchange of all H)
1	Decahydronaphthalene (trans)	0.086	0.028	4	1490	4370	80	1.8
2	Decahydronaphthalene (trans)	0.053	0.020	32	1360	3770	91	2.4
3	Decahydronaphthalene (30% cis + 70% trans)	0.049	0.025	11.5	309	683	18	2.6

We have previously suggested that hydrogen exchange with saturated hydrocarbons in presence of sulfuric acid proceeds by a chain mechanism [2]. For the further development of this idea it was of interest to study the exchange reactivity of mixtures of hydrocarbons having tertiary carbons with hydrocarbons that do not contain a tertiary carbon. If in a hydrogen-exchange reaction initiated by a hydrocarbon having a tertiary carbon atom the chain can be propagated via primary and secondary carbon atoms, then the hydrocarbon that does not contain a tertiary carbon will evidently be drawn into the reaction.

In actual fact it was found that whereas the hydrocarbon having a tertiary carbon underwent almost complete hydrogen exchange, the added hydrocarbon that had no tertiary carbon did not enter the exchange reaction. Thus it was found that, when a mixture of n-heptane and methylcyclohexane was treated with heavy sulfuric acid, only the methylcyclohexane underwent hydrogen exchange, the n-heptane being unaffected. These results indicate that the chain is propagated only via tertiary carbon atoms.

EXPERIMENTAL*

1. Cyclohexane and Heavy (Deuterium-rich) Sulfuric Acid. Cyclohexane was prepared by the hydrogenation of repeatedly frozen commercial benzene in an autoclave in presence of a nickel catalyst. The cyclohexane was distilled through a 40-plate column, and was then purified by passage through a column of silica gel. The constants of the cyclohexane were: b.p. 80.4-80.5° (750 mm); d_4^{20} 0.7782; and n_D^{20} 1.4263.

A mixture of 2.73 g (0.033 mole) of cyclohexane and 4.85 g (0.050 mole) of heavy sulfuric acid** (density excess 96980 γ) was agitated in a sealed tube for three hours. After the experiment, the hydrocarbon was washed with 30% caustic potash and with water; it was then dried with potassium carbonate and distilled over sodium. After the experiment the constants of the hydrocarbon were: b.p. 80.2-80.5° (756 mm); n_D^{20} 1.4262; d_4^{20} 0.7788. The water obtained from the combustion of the cyclohexane had a density excess of 272 γ; if all of the twelve hydrogen atoms had undergone exchange with deuterium, the density excess would have been 19,350 γ. The results show that practically no hydrogen exchange occurred between cyclohexane and heavy sulfuric acid.

2. Methylcyclohexane and Heavy Sulfuric Acid. Methylcyclohexane was prepared by the hydrogenation of toluene, which was first purified by conversion into p-toluenesulfonic acid, recovery by hydrolysis, and distillation through a 30-plate column. The hydrogenation was performed in an autoclave in presence of a nickel catalyst. The methylcyclohexane was purified by passage through a silica-gel column, and was then distilled through a 30-plate column. The constants of the methylcyclohexane were: b.p. 100.3-100.4°, (760 mm); d_4^{20} 0.7696; n_D^{20} 1.4230.

A. A mixture of 2.65 g (0.027 mole) of methylcyclohexane and 5.36 g (0.054 mole) of heavy sulfuric acid (96,980 γ) was agitated in a sealed tube for three hours. After the experiment, the hydrocarbon was treated as in Expt. 1, and the final constants of the hydrocarbon were: b.p. 99.5-100° (748 mm); d_4^{20} 0.7914; n_D^{20} 1.4220. The value found for the density excess of the combustion water from the methylcyclohexane was 20,915 γ; value calculated for exchange of all hydrogens with deuterium: 21,418 γ.

B. A mixture of 2.87 g (0.029 mole) of methylcyclohexane and 5.76 g (0.058 mole) of heavy sulfuric acid (96,980 γ) was agitated for 10 hours 30 minutes. After the experiment the constants of the hydrocarbon were: b.p. 99-99.5° at 736 mm; d_4^{20} 0.7914; n_D^{20} 1.4220. The value found for the density excess of the combustion water from the methylcyclohexane was 20,650 γ; value calculated for exchange of all hydrogens: 21,290 γ.

C. A mixture of 2.12 g (0.022 mole) of methylcyclohexane and 5.27 g (0.053 mole) of heavy sulfuric acid (96,980 γ) was agitated for 26 hours. After the experiment the constants of the hydrocarbon were: b.p. 98.5-99.5° at 748 mm; d_4^{20} 0.7971; $n_D^{20.1}$ 1.4220. The value found for the density excess of the combustion water from the methylcyclohexane was 24,890 γ; value calculated for exchange of all hydrogens: 25,060 γ.

The results of Experiments A, B, and C indicate that all the hydrogen atoms enter into the exchange reaction and that exchange equilibrium is established already in three hours.

3. trans-1,4-Dimethylcyclohexane and Heavy Sulfuric Acid. trans-1,4-Dimethylcyclohexane was prepared by the hydrogenation of p-xylene, obtained by the careful purification of the commercial product by repeated freezing. The hydrogenation was performed in presence of platinized charcoal. The 1,4-dimethylcyclohexane was purified by passage through a silica-gel column and distillation through a 75-80-plate column. The fraction taken for investigation had b.p. 119.5° (761 mm); d_4^{20} 0.7627; n_D^{20} 1.4209, which correspond to the constants of trans-1,4-dimethylcyclohexane.

* A. N. Martynova took part in the experimental work.

** The preparation of the heavy sulfuric acid is described in the previous communication.

A mixture of 2.24 g (0.020 mole) of trans-1,4-dimethylcyclohexane and 8.98 g (0.040 mole) of heavy sulfuric acid (15,990 γ) was agitated in a sealed tube for 12 hours. After the experiment the hydrocarbon was purified in the usual way, and had d_4^{20} 0.7686, $n_D^{20.2}$ 1.4220. The value found for the density excess of the combustion water from the trans-1,4-dimethylcyclohexane was 3214 γ.* The results show that all of the hydrogen atoms of 1,4-dimethylcyclohexane took part in the exchange reaction, but it appears that, under the conditions of the experiment, the hydrocarbon underwent isomerization (evidenced by the change in the constants of the hydrocarbon).

4. 1-Ethyl-4-methylcyclohexane and Heavy Sulfuric Acid. 1-Ethyl-4-methylcyclohexane was prepared as follows: p-toluidine, purified by two recrystallizations from isooctane, was converted by the Sandmeyer reaction into p-bromotoluene, which was then converted into 1-ethyl-4-methylbenzene by the Wurtz reaction; this was then hydrogenated in presence of platinized charcoal at 175°. The hydrogenated product was purified by passage through a silica-gel column and distillation through a 75-80-plate column. The fraction taken for investigation (intermediate between the cis and trans isomers) boiled over the range 149.3-152.2° (760 mm); d_4^{20} 0.7851; n_D^{20} 1.4326.

A. A mixture of 2.36 g (0.019 mole) of 1-ethyl-4-methylcyclohexane and 5.85 g (0.058 mole) of heavy sulfuric acid (94,000 γ) was agitated for 11 hours. After the experiment the hydrocarbon was purified in the usual way, and its constants were $d_4^{20.1}$ 0.8064; $n_D^{20.1}$ 1.4302. The value found for the density excess of the combustion water was 20,100 γ, and the value calculated for exchange of all seventeen hydrogens was 24,232 γ.

B. A mixture of 1.50 g (0.012 mole) of 1-ethyl-4-methylcyclohexane and 5.36 g (0.054 mole) of heavy sulfuric acid (16,000 γ) was agitated for 25 hours. After the experiment the constants of the hydrocarbon were d_4^{20} 0.7884; n_D^{20} * 1.4312. The value found for the density excess of the combustion water was 5176 γ, and the value calculated for exchange of all seventeen hydrogens was 5390 γ.

From these results it will be seen that exchange equilibrium between 1-ethyl-4-methylcyclohexane and heavy sulfuric acid is established more slowly than for methylcyclohexane and heavy sulfuric acid and that, under these conditions, exchange is apparently accompanied by partial isomerization of the hydrocarbon.

5. 1,1-Dimethylcyclohexane and Heavy Sulfuric Acid. 1,1-Dimethylcyclohexane was prepared by the hydrogenation of dimedon [3]. The hydrocarbon was purified by distillation through a 40-plate column, and its constants were: b.p. 119.9° (760 mm); d_4^{20} 0.7810; n_D^{20} 1.4294. A mixture of 1.74 g (0.016 mole) of 1,1-dimethylcyclohexane and 5.05 g (0.051 mole) of heavy sulfuric acid was agitated for four hours. After the experiment the purified hydrocarbon had the following constants: d_4^{20} 0.7819; $n_D^{20.3}$ 1.4293. The value found for the density excess of the combustion water was 89 γ, and the value calculated for exchange of all 16 hydrogen atoms was 5000 γ. These results indicate that 1,1-dimethylcyclohexane does not undergo hydrogen exchange with heavy sulfuric acid.

6. Cyclopentane and Heavy Sulfuric Acid. Cyclopentane was prepared by the method developed by Kazansky, Terentyeva, and Bulanova [4]. It was distilled through a 40-plate column, and its constants were: b.p. 49.0° (760 mm); d_4^{20} 0.7452; n_D^{20} 1.4065.

A. A mixture of 3.80 g (0.054 mole) of cyclopentane and 5.80 g (0.059 mole) of heavy sulfuric acid (17,000 γ) was agitated for one hour. After the experiment the hydrocarbon was purified in the usual way and had the following constants: b.p. 48.5-49.0° (750 mm); d_4^{20} 0.7456; $n_D^{20.6}$ 1.4062. The value found for the density excess of the combustion water from the cyclopentane was 56 γ, and the value calculated for exchange of all ten hydrogen atoms was 2980 γ.

B. A mixture of 1.56 g (0.022 mole) of cyclopentane and 4.24 g (0.042 mole) of heavy sulfuric acid (15,300 γ) was agitated for three hours. The value found for the density excess of the combustion water was 98 γ, and the value calculated for exchange of all hydrogen atoms was 4193 γ.

C. A mixture of 1.95 g (0.028 mole) of cyclopentane and 4.38 g (0.045 mole) of heavy sulfuric acid was agitated for 50 hours. After the experiment the constants of the hydrocarbon were: 48.5-49° (751 mm); n_D^{20} 1.4062; d_4^{20} 0.7451. The value found for the density excess of the combustion water was 94 γ, and the value calculated for exchange of all hydrogen atoms was 3719 γ.

The results of Experiments A, B, and C indicate that, even when contact with heavy sulfuric acid is prolonged, cyclopentane undergoes practically no hydrogen exchange.

7. Methylcyclopentane and Heavy Sulfuric Acid. Methylcyclopentane was prepared by isomerization of cyclohexene in presence of aluminum oxide into methylcyclopentenes [5], which were then distilled through a 35-plate column and hydrogenated at room temperature in presence of a platinum catalyst. The hydrogenation product was purified by distillation through a 50-plate column. The constants of the methylcyclopentane were: b.p. 71.8° (760 mm); n_D^{20} 1.4098; d_4^{20} 0.7485. Samples of methylcyclopentane were shaken with heavy sulfuric acid of

* The value calculated for exchange of all hydrogens was 3228 γ.

various deuterium contents for various times. After the experiments the hydrocarbon was purified in the usual way and was subjected to combustion over copper oxide. The course of the hydrogen-exchange reaction was characterized by the value of the density excess of the combustion water. The results of the experiments are given in Table 5; they show that exchange equilibrium between methylcyclopentane and heavy sulfuric acid is established in 14-15 hours.

TABLE 5

Expt. No.	Amt. (moles) of substance taken for reaction		Equiv. density excess of acid (γ)	Duration of reaction (hr)	Constants of hydrocarbon		Density excess of combustion water of hydrocarbon (γ)		Exchange (% of value calcd. for exchange of all hydrogen)
	methylcyclopentane	heavy sulfuric acid			n_D^{20}	d_4^{20}	calcd. for all H	found	
1	0.035	0.021	4136	1	–	–	378	202	54
2	0.033	0.060	17000	1	–	–	4014	2118	53
3	0.046	0.046	17000	2.5	–	–	2399	1578	66
4	0.027	0.047	15300	3	1.4100	0.7507	3362	2526	75
5	0.027	0.041	15500	4	–	–	3117	2590	83
6	0.033	0.060	15000	5	–	–	3386	2926	90
7	0.018	0.048	15300	10	1.4097	0.7539	4507	4214	94
8	0.020	0.063	15300	15	1.4095	0.7536	5289	5068	96
9	0.024	0.062	16000	14	–	–	4848	4807	99

8. Decahydronaphthalene and Heavy Sulfuric Acid. A. trans-Decahydronaphthalene, having the constants b.p. 72.0-72.5° at 18 mm; d_4^{20} 0.8690; n_D^{20} 1.4692, was prepared by isomerization of commercial decahydronaphthalene in presence of aluminum chloride [6]. The isomerizate was distilled through a 35-plate column. A mixture of 3.80 g (0.028 mole) of trans-decahydronaphthalene and 8.44 g (0.086 mole) of heavy sulfuric acid (17,000 γ) was agitated for four hours. After the experiment the constants of the hydrocarbon were: b.p. 184-184.5° (737 mm); n_D^{20} 1.4689. The value found for the density excess of the combustion water was 80 γ, and the value calculated for exchange of all hydrogen atoms was 4371 γ.

B. A mixture of 2.85 g (0.020 mole) of trans-decahydronaphthalene and 5.23 g (0.053 mole) of heavy sulfuric acid (17,000 γ) was agitated for 32 hours. After the experiment the constants of the hydrocarbon were: b.p. 55.7-56.2° (8 mm); d_4^{20} 0.8696; $n_D^{20.3}$ 1.4689. The value found for the density excess of the combustion water was 91 γ, and the value calculated for exchange of all hydrogen atoms was 3772 γ.

It may be concluded on the basis of the results of Experiments A and B that trans-decahydronaphthalene does not undergo hydrogen exchange with heavy sulfuric acid to any appreciable extent.

C. A mixture of 3.38 g (0.025 mole) of decahydronaphthalene containing 30% of the cis and 70% of the trans isomer* (b.p. 59.6-62.0° at 10 mm; n_D^{20} 1.4739) and 4.91 g (0.049 mole) of heavy sulfuric acid (4136 γ) was agitated for 11 hours 30 minutes. The value found for the density excess of the combustion water from the decahydronaphthalene was 18 γ, and the value calculated for exchange of all hydrogen atoms was 683 γ.

These results indicate that neither decahydronaphthalene isomer takes part in a hydrogen-exchange reaction.

9. Treatment of a Mixture of Methylcyclohexane and n-Heptane with Heavy Sulfuric Acid. A. A mixture of 0.95 g of methylcyclohexane, 0.82 g of n-heptane, and 5.75 g of heavy sulfuric acid (16,000 γ) was agitated in a sealed tube for 11 hours. The value found for the density excess of the combustion water obtained from the mixture of hydrocarbons was 3674 γ, and the values calculated were 4766 γ for exchange with both hydrocarbons, and 3698 γ for exchange only with methylcyclohexane.

B. A mixture of 0.88 g of methylcyclohexane, 0.76 g of n-heptane, and 4.26 g of heavy sulfuric acid (16,000 γ) was agitated for 50 hours. The value found for the density excess of the combustion water was 3328 γ, and the values calculated were 3317 γ for hydrogen exchange with methylcyclohexane and 4450 γ for exchange with both hydrocarbons.

These results show that only the methylcyclohexane takes part in the exchange reaction.

* The composition of the mixture was determined from the refractive index [7].

We express our deep gratitude for samples of pure hydrocarbons from A. F. Plate (methylcyclopentane and trans-decahydronaphthalene), O. D. Sterligov (cyclohexane, methylcyclohexane, mixture of decahydronaphthalene isomers), and T. F. Bulanova (cyclopentane).

SUMMARY

1. A study has been made of the hydrogen-exchange reaction occurring when heavy sulfuric acid reacts with saturated cyclic hydrocarbons (cyclohexane, methylcyclohexane, 1,1-dimethylcyclohexane, 1,4-dimethylcyclohexane, 1-ethyl-4-methylcyclohexane, cyclopentane, methylcyclopentane, and cis- and trans-decahydronaphthalenes).

2. It has been established that monocyclic hydrocarbons containing tertiary carbon atoms (methylcyclohexane, 1,4-dimethylcyclohexane, 1-ethyl-4-methylcyclohexane, and methylcyclopentane) undergo hydrogen exchange, equilibrium being established in a few hours at room temperature.

3. It has been found that no hydrogen exchange is to be observed between heavy sulfuric acid and cis- and trans-decahydronaphthalenes.

4. It has been established that, when a mixture of a hydrocarbon containing a tertiary carbon atom with a hydrocarbon that does not contain a tertiary carbon atom is treated with heavy sulfuric acid, only the hydrocarbon containing the tertiary carbon atom takes part in hydrogen exchange.

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Institute of Organic Chemistry of the
USSR Academy of Sciences

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• See Consultants Bureau Translation, page 931.

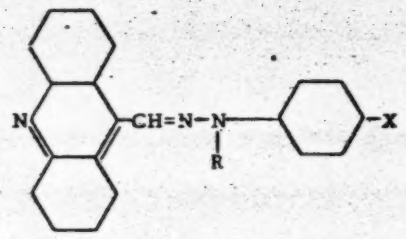
ABSORPTION SPECTRA AND MOLECULAR STRUCTURE

ANALOGOUS BEHAVIOR OF AZO AND IMINO GROUPS

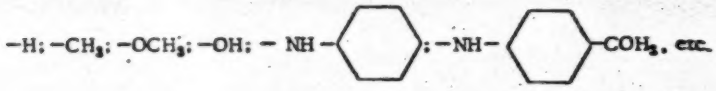
A. A. Kharkharov

It is well known that the replacement in the benzene molecule of $-CH=CH-$ by $-NH-$, $-O-$, or $-S-$ gives hetereocyclic compounds that retain properties of aromatic compounds. The present view on the aromatic character of these substances is based on the idea that four electrons from the double bonds and two electrons of the hetero atom form a system that is particularly stable [1, 4]. There is wide acceptance also for the concept of the conjugation of the free electron pairs of the hetero atoms of terminal nucleophilic substituents ($-NR_2$, $-OR$, $-Hal$ etc.) with the π-electrons of aromatic, heterocyclic, and open-chain compounds, as, for example, in aniline, 2-aminopyridine, and acetamide [2, 3, 4].

Recently the concept introduced by Nesmeyanov of the conjugation of single bonds has received general acceptance [4]. We have observed [5] a peculiar case of conjugation in the arylhydrazones of some heterocyclic aldehydes, for example of the type:



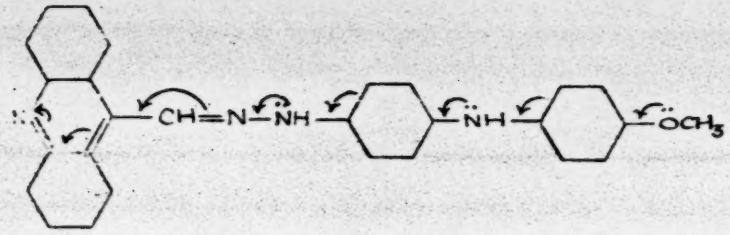
where R = $-H$; $-C_2H_5$, X = $-NO_2$; $-COOH$; $-C\begin{matrix}O\\H\end{matrix}$; $-SO_3H$; $-H$; $-CH_3$; $-OCH_3$; $-OH$;



$-H$; $-CH_3$; $-OCH_3$; $-OH$; $-NH-$; $-NH-$ $-COH_3$, etc.

The peculiarity of systems of this kind is that the acridine nucleus is conjugated with the substituent X via the π-electrons of the $-C\begin{matrix}\\H\end{matrix}=N-$ group and the benzene ring, which are separated from one another by a group ($-NH-$) that is bound to neighboring atoms by means of two single bonds. The interaction of the π-electrons is here effected with the participation of the free electron pair of the hetero atom.

The presence of such conjugation in the molecule is indicated, above all, by the color of these compounds. Even the bases of such compounds have intense yellow, orange, or brown colors; and they have characteristic absorption spectra. The position of the maximum of the main absorption band of arylhydrazones of 9-acridinecarboxaldehyde depends on the structure of the substituent (Fig. 1). The hetero atom of the acridine ring system, owing to its electrophilic character, causes a redistribution of electron density in the conjugated chain. In particular, the direction of this redistribution may be shown for the p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (see following page):



The effect of the substituent, as will be seen from the curves given in Fig. 1, is however insufficiently clearly expressed in this case. The bathochromic effect of substituents has a particularly strong influence on the color of salts of these bases. For example, salt formation in the case of the compound cited above (II) is accompanied by displacement of the absorption maximum from 485 to 715 mμ (II and VIII, cf. Fig. 1 and 3), and in the case of the p-nitrophenylhydrazone of 9-acridinecarboxaldehyde (I) – from 444 to 522 mμ (I and VI, Fig. 1 and 3).

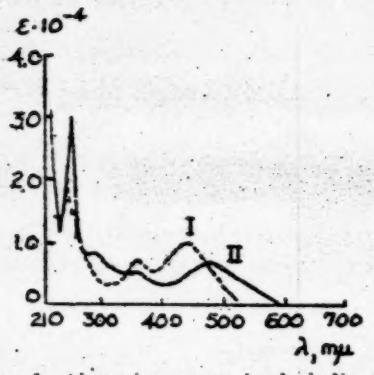
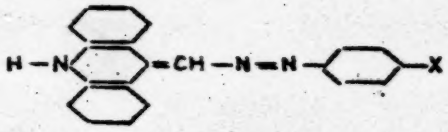


Fig. 1. Absorption spectra in alcoholic solution: ----- p-nitrophenylhydrazone of 9-acridinecarboxaldehyde (I); — p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (II).

The monoacid salts of compounds of this type behave as typical dyes: they are not only intensely colored, but also have the ability to dye textile fibers. These properties can only be possessed by such compounds when the substituent X is conjugated with the acridine ring system. It might be thought that substances of this kind have not the hydrazone, but the azo structure:



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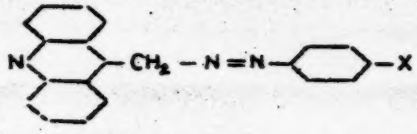
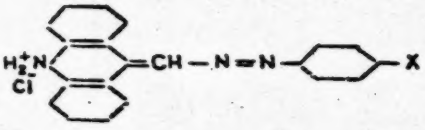


and their salts, correspondingly:



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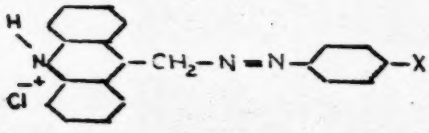


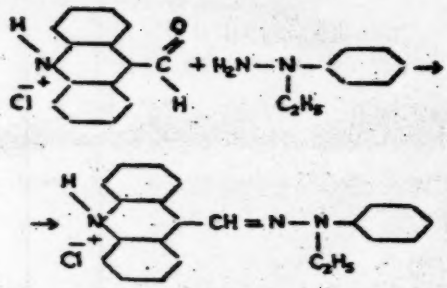
In the first case the nucelophilic group would be conjugated with the long electrophilic chain of alternating double and single bonds, and in the second case we should have a nonconjugated system, in which the electrophilic group would be isolated from the nucleophilic methylene group. The investigations of Izmailsky and coworkers have

shown that some nonconjugated systems of the diphenylmethane type containing electrophilic and nucleophilic substituents in different rings are colored, in spite of the absence of conjugation. However, unlike the compounds cited below, substances of this sort cannot have a very deep color. The color of compounds having nonconjugated systems is not generally deeper than red, and it never attains blue or green.

The bases of the substances that we are describing are also highly colored, but among their salts with acids and bases there are some compounds having absorption maxima almost at the infrared limit of the spectrum (see, for example, Fig. 3, for the substance (VIII), $\lambda_{max} = 715$). The nature of the effect of substituents does not depend on the hydrogen ion concentration.

It is doubtful whether molecular complexes can be stable both in acid and in alkaline media. The main feature, however, distinguishing the nonconjugated systems studied by Izmailsky [6-16] and molecular complexes [16-18] from our compounds is that the former are not dyes having affinity for protein and cellulose fibers. It should be noted that, in accord with the ideas developed in this paper, dyes of the Variamine Blue type must be assigned not to the nonconjugated group, but to the group of systems in which conjugation occurs through $-NH-$.

In order to exclude the possibility of the azo structure, we prepared the ethylphenylhydrazone of 9-acridinecarboxaldehyde, which is incapable of isomerization, by the reaction:



Comparison of the absorption curves of the ethylphenylhydrazone and phenylhydrazone of 9-acridinecarboxaldehyde (Fig. 2) showed that these substances have completely analogous structures. The substances that we have studied, therefore, have the hydrazone, and not the azo, structure.

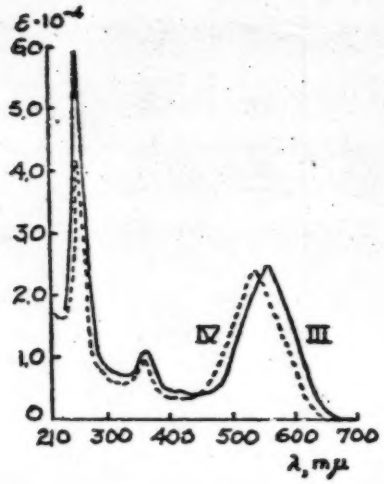


Fig. 2. Absorption spectra of hydrochlorides in alcoholic solution: — phenylhydrazone of 9-acridinecarboxaldehyde (III); ----- ethylphenylhydrazone of 9-acridinecarboxaldehyde (IV).

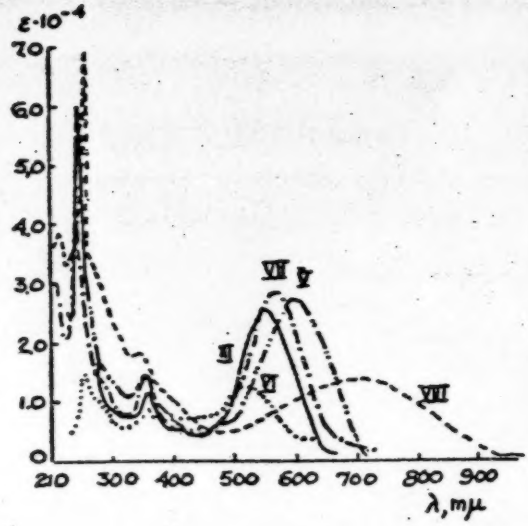
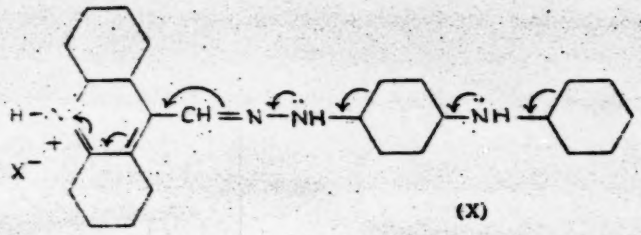


Fig. 3. Absorption spectra of solutions of hydrochlorides in alcoholic HCl: — phenylhydrazone of 9-acridinecarboxaldehyde (III); — ··· — ··· — p-methoxyphenylhydrazone of 9-acridinecarboxaldehyde (V); . . . . p-nitrophenylhydrazone of 9-acridinecarboxaldehyde (hydrochloride of I), (VI); — · · — · · — p-phenylazophenylhydrazone of 9-acridinecarboxaldehyde (VII); —— p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (hydrochloride of II) (VII

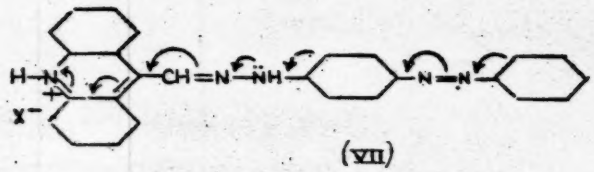
The great deepening of color on passing from the bases of arylhydrazones of 9-acridinecarboxaldehyde to their salts is to be explained as follows: the addition of a proton to the free electron pair of the acridine nitrogen intensifies its electrophilic properties and therefore its influence on the substituent X.

As we have already indicated, the nature of the substituent X in the aromatic nucleus attached through $-NH-$ has a very great influence on the color of the compound (Fig. 3). Thus, when X = H (III), λ_{max} of the main absorption band is 562 mμ; when X = NO_2 (VI), the absorption maximum is displaced towards the shorter waves (λ_{max} = 522 mμ), and when X = OCH_3 (V) it is displaced towards the longer waves (λ_{max} = 610 mμ).



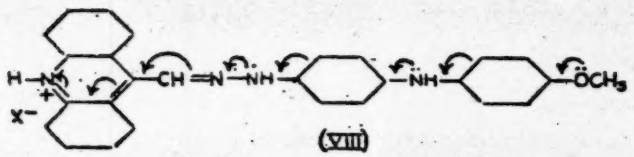
(X)

A particularly powerful bathochromic effect is shown by the substituent X = $-NH-C_6H_5$ (X)[(λ_{max} = 675 mμ, see Fig. 4)]. It displaces the absorption band much more into the long-wave part of the spectrum than the substituent $-N=N-C_6H_5$ (VII) (λ_{max} = 579 mμ, see Fig. 4).



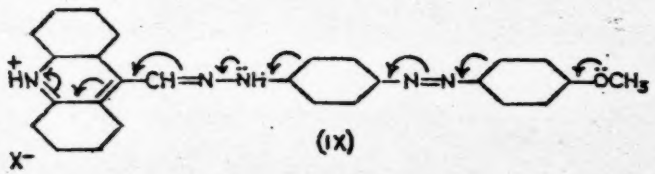
(VII)

The color of these compounds (VII and X) is associated, above all, with the presence in their molecules of long conjugated chains. Of the compounds that we have prepared, the deepest color is possessed by the p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (VIII, λ_{max} = 715 mμ; see Fig. 4) in which the OCH_3 group is



(VIII)

conjugated with the acridine nitrogen through the longest chain, which contains two $-NH-$ groups. The maximum of the main absorption band of this compound is shifted much more towards the longer waves than that of the p-(p-methoxyphenylazo)phenylhydrazone of 9-acridinecarboxaldehyde (IX, λ_{max} = 590 mμ see Fig. 4), in which the azo group participates in the conjugation.



(IX)

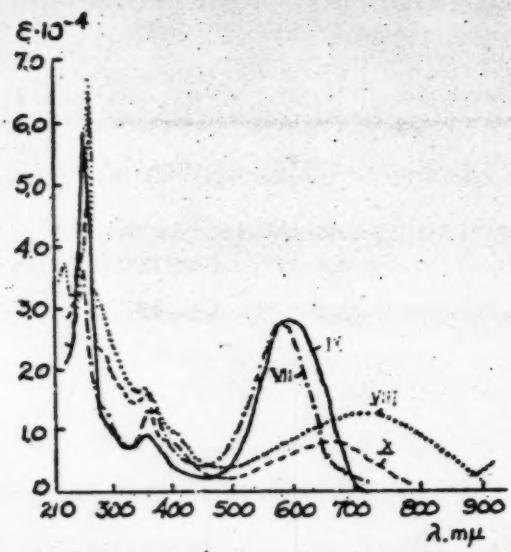


Fig. 4. Absorption spectra of solutions of hydrochlorides in alcoholic HCl: — · — · — p-phenylazophenylhydrazone of 9-acridinecarboxaldehyde (VII); . . . . p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (VIII); — p-(p-methoxyphenylazo)phenylhydrazone of 9-acridinecarboxaldehyde (IX); ---- p-anilinophenylhydrazone of 9-acridinecarboxaldehyde (X).

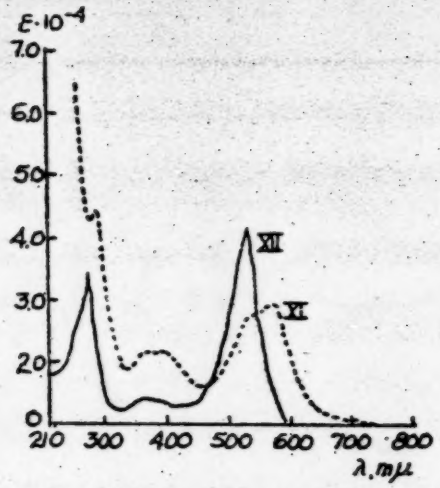
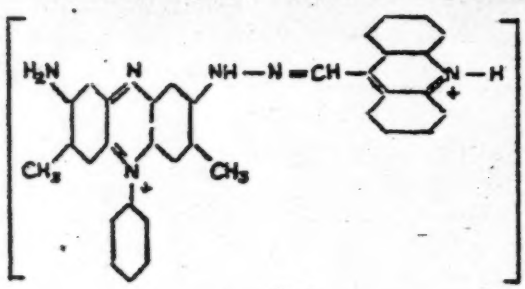


Fig. 5. Absorption spectra of solutions of the hydrochlorides of the compound (XI) and of Safranine T (XII) in alcoholic HCl.

In both cases the introduction of an OCH_3 group has a bathochromic effect. This indicates that in the systems under examination replacement of an azo group by an imino group not only does not interrupt the conjugation of the chain, but even intensifies it. A still more convincing proof that the replacement of an azo or other double-bonded grouping by the imino group does not interrupt the conjugation is provided by the substantive properties of some members of this class of dyes.

A dye that we have prepared (XI, λ_{max} = 570 mμ; see Fig. 5)•:



(XI)

not only has a deeper color than Safranine T (XII, λ_{max} = 535 mμ), but differs from it also in being able to dye cellulose fibers (cotton, viscose and cuprammonium rayons) directly from aqueous solution without the use of a mordant. As Porai-Koshits, Bogoslovsky, and others (19-22] have shown, this property is generally possessed by only

• The author's formula is correctly transcribed, here, although the fact that the dye is compared with Safranine T suggests that the phenyl group should be attached to the other N of the phenazine ring system. —Publisher.

these dyes that contain a long chain of alternating single and double bonds. If the $-NH-$ group interrupted the conjugated chain, then the compound (XI) could not have affinity for cellulose fibers.

The information on the absorption spectra of arylhydrazones of 9-acridinecarboxaldehydes is published for the first time. The dye Safranine, taken for comparison and measured under like conditions, forms an exception. The spectrophotometric measurements were carried out in an SF-1 photoelectric apparatus. The solvents used were a 0.2 N solution of HCl in ethanol and pure (96%) ethanol.

SUMMARY

1. The experimental data presented in this paper show that the replacement of $-N=N-$, and therefore other analogous groups, by $-NH-$ in certain conjugated systems does not interrupt the conjugation.

2. In the case of arylhydrazones of 9-acridinecarboxaldehyde this replacement is accompanied by a considerable shift of the maximum of the main absorption band towards the longer waves.

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ISOMERIZATION REACTIONS OF OLEFINIC HYDROCARBONS IN PRESENCE OF ALUMINOSILICATES

COMMUNICATION 2

A. A. Petrov

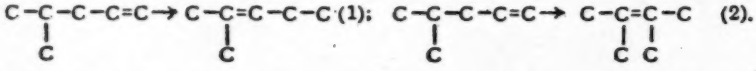
In the preceding communication we examined isomerization reactions of olefinic hydrocarbons, mainly of normal, or only slightly branched, structure [1]. It was shown that, in presence of an aluminosilicate catalyst, olefins of normal structure are readily isomerized to monoalkylalkenes, and in these migration of methyl side groups may occur in the main carbon chain. In order to explain the processes that occur, we made use of M. D. Lvov's hypothesis, according to which intermediate formation of alkylcyclopropanes occurs.

In the present paper we describe the continuation of this investigation, in which we have studied the isomerization of several new types of unsaturated hydrocarbons. We have examined, in particular, the following questions: 1) the possibility of the catalytic synthesis of dialkylalkenes from monoalkylalkenes, the examples taken being branched olefins in which the side methyl group is well removed from the double bond; 2) the stability of a quaternary carbon atom in olefinic hydrocarbons; 3) isomerization of cyclic olefinic hydrocarbons associated with a change in the number of carbon atoms in the ring; 4) disproportionation of carbon atoms of side chains of cyclic olefinic hydrocarbons; 5) confirmation of our previously proposed scheme of isomeric changes in olefins in presence of aluminosilicates, and its elaboration in greater detail by the application of new experimental data. The principal results of our investigation are given in Tables 1 and 2.

The conditions employed were the same as in the previously published work. Whatever hydrocarbon was taken, the products of the catalytic changes were found to consist not only of unsaturated hydrocarbons, but also of saturated hydrocarbons formed by the saturation of olefins in the course of a hydrogen-redistribution reaction. In this investigation our main attention was directed to the structure of the saturated hydrocarbons obtained, but in certain cases we have separated the saturated and unsaturated parts of the catalyzate and studied them separately. The separation of the unsaturated hydrocarbons was effected by hydrogen bromide addition followed by conversion of the products via organomagnesium compounds to saturated hydrocarbons, and for this reason the hydrocarbons corresponding in structure to the unsaturated hydrocarbons of the catalyzate are given in the column headed "unsaturated part" in Table 1.

The results on the isomerization of cyclic olefinic hydrocarbons are given in Table 2. Since the saturation of cyclic olefins by the hydrogen-redistribution reaction proceeds considerably more readily than the saturation of aliphatic olefins, the experimental conditions were somewhat modified for the work on cyclic compounds. Also, only the saturated products, which in these cases formed the main bulk of the catalyzate, were investigated.

We shall now consider the results obtained. The first group of hydrocarbons investigated consisted of olefins in which there was an alkyl side group in a position remote from the double bond. In investigating the isomerization of hydrocarbons of this type, we wished to determine whether it was possible under the selected conditions for a second alkyl group to be formed at the double bond, or whether the double bond would migrate along the carbon chain until an olefin was formed having a tertiary double bond. In other words, according to which of the schemes below would hydrocarbons of this structural type react:



(1); (2).

As the experimental results show, the formation of a new alkyl group proceeds more rapidly than double-bond migration, and the isomerization products contain dialkylalkenes.

It is true that to some extent the double bond of the original hydrocarbon is apparently able to migrate towards the alkyl side group, and may even reach it. This process is indicated by the occurrence of 2-methylalkanes (2-methylpentane, 2-methylhexane, etc.) among the products obtained from hydrocarbons of this type. In general, these 2-methylalkanes can be regarded as saturated forms of the original hydrocarbons, without postulation of the occurrence of any isomeric change, but the frequently observed selective saturation of olefins having tertiary double bonds

TABLE 1

Isomerization Products of Olefins.

Experimental conditions: 250°, space velocity 0.2 liter/liter·hr; duration of experiment 100 minutes

No.	Original hydrocarbon	Composition of catalyzate	
		saturated part	"unsaturated part" (after conversion into saturated hydrocarbons)
1	4-Methyl-1-pentene	2-Methylpentane, 2,3-dimethylbutane	–
2	5-Methyl-1-hexene	2-Methylhexane, 2,4-dimethylpentane; in smaller amount 2,3-dimethylpentane	Composition same as saturated part
3	6-Methyl-1-heptene	2-Methylheptane, 2,5-dimethylhexane; in smaller amounts 2,4- and 2,3-dimethylhexanes	Composition same as saturated part
4	1-Heptene	2-Methylhexane, 3-methylhexane; a little 2,4-dimethylpentane	2-Methylhexane, 3-methylhexane
5	4,4-Dimethyl-1-pentene	2,3-Dimethylpentane, 2-methylhexane	–
6	2,3,3-Trimethyl-1-butene	2,2,3-Trimethylbutane, a little 2,4-dimethylpentane	Various amounts of 2,2,3-trimethylbutane and 2,4-dimethylpentane
7	1,5-Hexadiene	2-Methylpentane, a little 2,3-dimethylbutane	–
8	3-Ethyl-2-pentene	2-Methylhexane, 3-methylhexane, a little 2,4-dimethylpentane	–
9	2-Methyl-2-hexene	2-Methylhexane, 3-methylhexane, 2,4-dimethylpentane	–

NOTE: In the catalyzates from hydrocarbons No. 2 and 5 the presence of a certain amount of 3-methylalkanes was noted.

TABLE 2

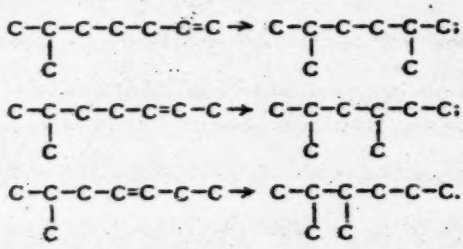
Isomerization Products of Cyclic Olefins

Experimental conditions: space velocity 0.6 liter/liter·hr; duration of experiment 100 minutes

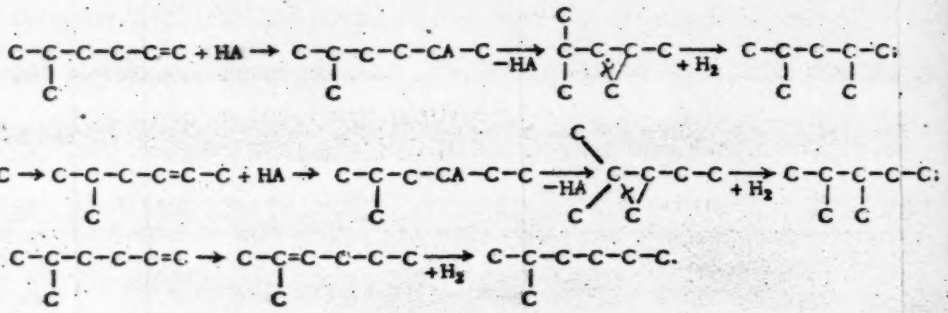
No.	Original hydrocarbon	Composition of catalyzate	
		in experiments at 250°	in experiments at 400°
1	1-Ethylcyclopentene	5-membered cycloalkanes 45%, methylcyclohexane 55%	Methylcyclohexane 27%, toluene 8%, 5-membered cycloalkanes 65% (mainly 1,3-dimethylcyclopentane)
2	1-Ethylcyclohexene	5-membered cycloalkanes 35%, 1,4-dimethylcyclohexane 65%	5-membered cycloalkanes 42%, aromatics 20% (xylenes), 6-membered cycloalkanes 38% (1,4-dimethylcyclohexane, a little 1,3-dimethylcyclohexane)
3	1-Propylcyclohexene	6-membered cycloalkanes 72%, 5-membered cycloalkanes 28%	–
4	Allylcyclohexane	6-membered cycloalkanes 64%, 5-membered cycloalkanes 36%	–
5	Allylbenzene	Monoalkylbenzene	–

under conditions of hydrogen redistribution compels us to postulate a preliminary migration of the double bond in these hydrocarbons. This supposition is supported also by the absence of olefins having a primary-secondary double bond in the products obtained from these same hydrocarbons.

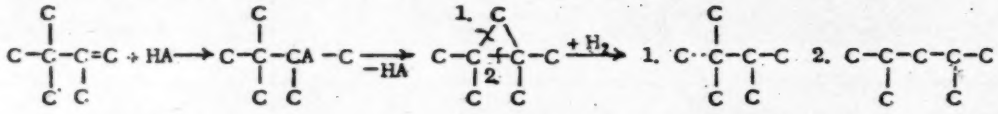
Finally, the occurrence of 2,4- and 2,3-dimethylhexanes in the 6-methyl-1-heptene catalyzate forms a clear proof of the migration of the double bond:



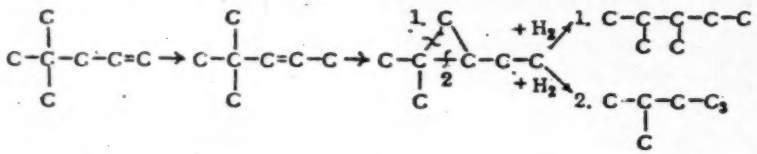
Transformations of hydrocarbons of this type can be expressed by the aid of our proposed mechanism in the following manner*:



The second group of hydrocarbons investigated were olefins having quaternary carbon atoms. In studying the transformations of hydrocarbons of this type, we tried to determine the circumstances under which the very vulnerable grouping at the quaternary carbon could be preserved under the conditions of aluminosilicate catalysis, or, in fact, of acid catalysis in general. Our results show that, when the double bond of the original hydrocarbon is attached to an alkyl side group (tertiary double bond), a quaternary grouping may be preserved. When, however, there is no tertiary double bond in the original hydrocarbon, a quaternary grouping is readily broken down. On the basis of our proposed scheme, the processes occurring may be represented as follows:



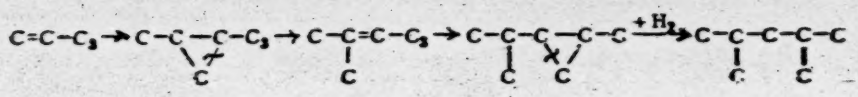
Formation of a certain amount of 2,4-dimethylpentane occurs as a result of rupture of the three-membered ring at the point marked "2". Similarly for 4,4-dimethyl-1-pentene:



We shall not consider the isomerization of 1-heptene, 3-ethyl-2-pentene, and 1,5-hexadiene in detail since their transformations are obviously covered completely by the above-described schemes.

We may add that 2-methylhexane is obviously formed from 1-heptene, and 3-methylhexane from 2-heptene, i.e., completely analogously to the transformations of 5-methyl-1-hexene. It is interesting that a certain amount of 2,4-dimethylpentane is formed from 1-heptene; this is probably formed in accordance with the following scheme:

* HA($HAlSiO_4$) denotes the aluminosilicate catalyst, which we are regarding as an acid having a hydrogen atom "H" that is capable of undergoing exchange with the hydrogen atoms of hydrocarbons.

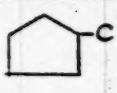


The conversion of 3-ethyl-2-pentene into 2-methylhexane probably goes with intermediate formation of 3-methyl-2-hexene.

In the cyclic olefin series isomerization is observed that may involve either expansion or contraction of the ring. It is interesting that, whereas the isomerization both of 1-methylcyclopentene and of 1-methylcyclohexene goes with difficulty (especially in the first case), the isomerization of the two corresponding ethylcycloalkenes goes considerably more readily. The ring-expansion reaction is particular marked in cyclopentanes. A similar readiness for cyclopentanes to react in presence of aluminum chloride was observed previously by Zelinsky and coworkers [2]. A characteristic feature of our results is that the composition of the final products (with respect to the content of five- and six-membered cycloalkanes) was approximately the same for all of the original hydrocarbons. The approximate ratio of five- and six-membered cycloalkanes was 1:2 (experiments at 250°).

At higher temperatures (Table 2) isomerization associated with ring expansion in cyclopentenes fell appreciably, a fact that is in general accord with the high stability of five-membered naphthenes at high temperatures. The data in the literature on the equilibrium of closely related hydrocarbons are given in Table 3 [3].

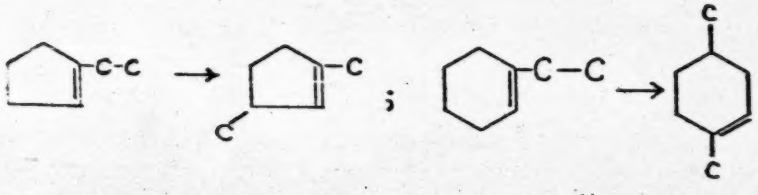
TABLE 3

Temperature (°C)	Composition of equilibrium mixture (%)			
				
250	79	21	—	—
300	84	16	34	66
400	90	10	94	6

It must be pointed out that in general, under the conditions of aluminisilicate catalysis, the composition of the mixture of isomerization products obtained is often far from the equilibrium value. This arises from the fact that the hydrogen-redistribution reaction that is proceeding simultaneously effects considerable changes in the composition of the isomerization product, saturating one or another form of hydrocarbon preferentially. This circumstance assumes even greater importance when we consider that paraffins and cycloparaffins are chemically inert under these conditions. The most characteristic example is found in a comparison of the isomerization of 1-methylcyclopentene and of 1-ethylcyclopentene. Since the six-membered isomer of the first hydrocarbon (cyclohexene) has a secondary double bond, and the corresponding isomer of the second hydrocarbon (methylcyclohexene) has a tertiary double bond, and since, under the conditions of aluminosilicate catalysis, hydrocarbons having tertiary double bonds are selectively saturated, it is found that the methylcyclopentene catalyzate consists only of methylcyclopentane, whereas the ethylcyclopentene catalyzate contains 55% of six-membered naphthenes.

Let us turn to the data presented in Table 2. From the approximately identical composition of the isomerization products of 1-propylcyclohexene and allylcyclohexane, we must suppose that the double bond readily migrates from the side chain to the ring. Similar ready migration of the double bond of allylcyclohexane in presence of a platinum catalyst has been noted previously by Levina [4]. Another proof of the formation of 1-propylcyclohexene from allylcyclohexane is afforded by the fact that in both hydrocarbons the hydrogen-redistribution reaction proceeds with approximately equal readiness; several times more readily than in aliphatic olefins [5].

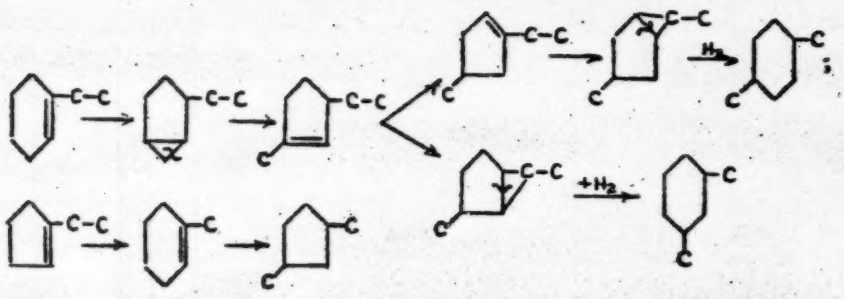
Of still greater interest, in our opinion, is another type of isomerization undergone by cyclic olefins, namely redistribution of radicals, proceeding as follows:



We have found that 1-ethylcyclohexene and, to a lesser extent, 1-ethylcyclopentene show this type of isomerization. A paper has recently appeared in which it is shown that isomerization of a similar type is undergone by isopropylcyclo-

hexene in presence of alumina impregnated in HCl [6]. In our experiments this sort of isomerization occurred very readily at 250° and at 400°.

In particular, all of the six-membered naphthenes of the 1-ethylcyclohexene catalyzate consisted of dimethylcyclohexanes. It is interesting that at 250° the sole isomerization product was 1,4-dimethylcyclohexane, and only in the 400° experiment was a comparatively small amount (20%) of 1,3-dimethylcyclohexane found. What is the mechanism of these transformations? Of the two possible schemes: a) alkylation of the ring by methyl radicals formed at the expense of the side chain, and b) several successive reactions involving ring formation, preference must be given to the second. Alkylation at atmospheric pressure and at such a low temperature (250°) for an aluminosilicate catalyst, requiring, moreover, the breakdown of an ethyl radical, is not very probable, all the more so since allylbenzene yields only monoalkylbenzene under these conditions, i.e., no redistribution of radicals occurs in a hydrocarbon that is, in general, much more readily alkylated. The most reasonable representation of isomerization of this type is as follows:



These schemes of ring transformations are very probable ones, for the individual stages are in themselves quite reasonable, and the experimental data (see Table 2) are in general agreement. The overall result is that we obtain the most stable forms of cyclopentene or cyclohexene hydrocarbons for the given conditions.

EXPERIMENTAL

Our investigation of the isomeric transformations of hydrocarbons was carried out in a continuous-flow system. The experimental conditions and the analytical procedure employed in the examination of the hydrocarbon mixtures have been published previously [1]. We shall give details of the investigation of products analyzed by methods different from those previously described; the products mainly concerned are those obtained from 1-ethylcyclohexene, which were analyzed by the oxidation of the dehydrogenated (in presence of platinized charcoal) C_8 fraction of the catalyzate. The oxidation was performed under the conditions described by Isagulyants and Egorova [7].

In the experiment at 250°, the appropriate operations (oxidation with $KMnO_4$) yielded crystals that sublimed without melting at above 240°. The elementary composition of these corresponded to that of the phthalic acids:

Found %: C 57.82; 57.67; H 3.77; 3.69; O 39.41; 39.64 (by difference)
Calculated %: C 57.85; H 3.64; O 38.53

The substance was boiled with methanol saturated with HCl (5%) and so converted into the dimethyl ester, which corresponded in melting point (139°) to dimethyl terephthalate.

In the experiment at 400° the same operations yielded crystals that again sublimed without melting and corresponded to the phthalic acids in elementary analysis:

Found %: C 57.88; 57.79; H 3.70; 3.63; O 39.42; 39.58 (by difference)

The methyl esters obtained melted over a wide range (120-139°), but the greater part of the product, obtained by recrystallization from ether, melted at 139°. By making use of the different solubilities of isophthalic and terephthalic acids in alcohol, we showed that our product contained about 70% of terephthalic acid. It was established

by the same method that oxidation of the saturated transformation products of allylbenzene yielded only benzoic acid (m.p. 123°).

The structures of the transformation products of the aliphatic hydrocarbons, and also of the five-membered cycloalkanes of the 1-ethylcyclopentene catalyzate, were established with the aid of Raman spectra.

The hydrocarbons required were obtained synthetically: by the Grignard reaction followed by dehydration of the tertiary alcohols by distillation with iodine, or by the Grignard-Wurtz reaction, according to the procedure developed by Kazansky and coworkers [8]. 4-Methyl-1-pentene was prepared by the condensation of isopropylmagnesium bromide with allyl bromide. 1,5-Hexadiene was prepared by Cortes' method from allyl bromide [9]. 5-Methyl-1-hexene was prepared by the condensation of isobutylmagnesium bromide and allyl chloride, and 1-heptene from butylmagnesium bromide and allyl bromide. 4,4-Dimethyl-1-pentene was prepared by the action of allyl chloride on tert-butylmagnesium chloride. 3-Ethyl-2-pentene was prepared from 1,1-diethyl-1-propanol, prepared by the Grignard method from ethylmagnesium bromide and propionic ester. 2,3,3-Trimethyl-1-butene was prepared from 1,1,2,2-tetramethyl-1-propanol, obtained from methylmagnesium iodide and pinacolone. 6-Methyl-1-heptene was prepared by the condensation of isopentylmagnesium bromide and allyl bromide. 1-Ethylcyclohexene and 1-propylcyclohexene were prepared from the corresponding alcohols, which were obtained by the Grignard method from cyclohexanone and ethyl- and propyl-magnesium bromides. 1-Ethylcyclopentene was prepared from the alcohol synthesized from ethylmagnesium bromide and cyclopentanone. Allylcyclohexane and allylbenzene were prepared by condensation of the corresponding alkylmagnesium bromides with allyl bromide. The constants of the hydrocarbons, after purification and fractionation through a 10-plate column are given in Table 4.

TABLE 4

Constants of Hydrocarbons

Hydrocarbon	B. p. (°C)	n_D^{20}	d_4^{20}	Bromine number
4-Methyl-1-pentene	53-54	1.3820	0.6683	185
1,5-Hexadiene	59-60	1.4040	0.6945	391
5-Methyl-1-hexene	84-85	1.3965	0.6926	165
1-Heptene	93-94	1.4000	0.7031	160
2-Methyl-2(1)-hexene	91-95	1.4070	0.7053	162
3-Ethyl-2-pentene	93-95	1.4150	0.7210	167
4,4-Dimethyl-1-pentene	71-72	1.3925	0.6991	162
2,3,3-Trimethyl-1-butene	77-79	1.4025	0.7060	164
6-Methyl-1-heptene	112-114	1.4065	0.7121	142
1-Ethylcyclopentene	104-106	1.4420	0.7989	179
1-Ethylcyclohexene	134-136	1.4566	0.8290	141
1-Propylcyclohexene	150-152	1.4580	0.8410	110
Allylcyclohexane	148-151	1.4507	0.8088	118
Allylbenzene	157-159	1.5112	0.8930	134

The author takes this opportunity of expressing his deep gratitude to G. D. Galpern and A. N. Kislitsky for carrying out the spectroscopic investigations.

SUMMARY

1. In presence of an aluminosilicate catalyst at 250°, acyclic and cyclic olefin hydrocarbons undergo considerable structural changes, which are readily explained by means of a mechanism scheme in which the intermediate formation of cyclopropane derivatives is postulated. The following are the most characteristic types of isomeric transformations: 1) isomerization of normal olefins into monoalkylalkenes in which the alkyl group stands at the double bond; 2) formation of dialkylalkenes from monoalkylalkenes in which the alkyl side group is well removed from the double bond; 3) breakdown of a grouping at a quaternary carbon atom, except in those cases in which, in addition to a quaternary carbon, there is a tertiary carbon at the double bond; 4) in the isomerization of C_7 (and higher) cycloalkenes, a mixture of two parts of six-membered and one part of five-membered naphthenes is formed; 5) in hydrocarbons having a primary-secondary double bond, migration of the double bond so as to form unsymmetrically substituted ethylene derivatives readily occurs; 6) reduction in the number of carbon atoms in alkyl side groups occurs.

2. The overall result of the catalytic transformations of olefinic hydrocarbons in presence of aluminosilicate should be regarded as the summative effect of isomerization and hydrogen-redistribution processes, and the unsaturated hydrocarbons that are mainly formed are those which have the least tendency to undergo isomerization under the experimental conditions and which are readily saturated at a later stage owing to the redistribution of hydrogen. The most characteristic forms of saturated C_6–C_8 hydrocarbons obtained at 250° we consider to be: 2-methylalkanes; 2,3-, 2,4-, and 2,5-dimethylalkanes; methylcyclopentane; methylcyclohexane; and also 1,3-dimethylcyclopentane and 1,4-dimethylcyclohexane.

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CONDUCTIVITY OF ACID CATALYSTS; AND ITS VARIATION DURING ALKYLATION AND POLYMERIZATION REACTIONS

Ya. M. Paushkin and M. V. Kurashev

One of the fundamental properties of acid catalysts is the electrical conductivity associated with the ionic character of acids. According to modern views, acid catalysis is to be explained by the ability of acids to dissociate into ions, which take part in the intermediate stages of the reaction. The mechanism of alkylation (I) and polymerization (II) with the participation of protons may be represented by the following scheme [1]:

$$(CH_3)_2C{=}CH_2 + H^+ \rightarrow (CH_3)_3C^{\oplus} \xrightarrow{C_4H_8} C_8H_{17}^{\oplus} \begin{cases} \xrightarrow{i\,C_4H_{10}} C_8H_{18} + (CH_3)_3C^+ & \text{(I)} \\ \xrightarrow[C_4H_8]{} C_8H_{16} + H^+ & \text{(II)} \end{cases}$$

Reaction is initiated by addition of a proton at a double bond, which leads to the formation of a tert-butyl carbonium ion. This carbonium ion then adds to 2-methylpropene with formation of a C_8H_{17} carbonium ion, which, depending on the reaction conditions, may be converted in presence of isobutane into an octane isomer and a carbonium ion (alkylation), or may be converted into an octene isomer (polymerization) with elimination of a proton.

In connection with the participation of ions in the reaction, it is of interest to investigate the conductivity of acid catalysts as a supplementary physicochemical parameter that gives an indication of the variation of the properties of the catalyst, particularly its ionic character, in the course of the reaction. Volkenshtein [2] points out that catalytic activity, like conductivity, must be assigned to the category of "structure-sensitive" properties of heterogeneous catalysts. There is a relationship between the catalytic activity of a semiconductor and its conductivity, i.e., between the rate constant for the reaction and the conductivity of the catalyst κ at a given temperature, and it may be represented by the function:

$$k_T = k\varphi(\kappa_T).$$

The conductivity can serve as a characteristic of the activity only insofar as we are concerned with various samples of the same catalyst differing in the content of an additive that does not affect the general nature of the catalyst. The specific conductivity of liquid electrolytes is determined by the concentration of ions and their mobility:

$$\kappa = c(u + v),$$

in which κ is the specific conductivity, c is the ionic concentration, and u and v are the ionic mobilities, i.e., the product of charge and velocity. The mobility of the hydrogen ion is 313 coulomb·cm/sec, and those of the ions F^-, NO_3^-, and $\frac{1}{2}SO_4^-$ vary over the range 46.6-67 coulomb·cm/sec.

For heterogeneous catalysts a direct relationship has been established purely theoretically between catalytic activity and the conductivity of the catalyst. If acid catalysis were due directly to free protons, it would be possible to find a relationship between conductivity and catalytic activity.

As will be seen below, however, no general relationship is to be observed between the conductivity and activity of acid catalysts. This may be explained by the fact that protons are not met in the free state in anhydrous acids, but are combined in the form of complex ions of the type $[H_2X]^+$. The formation of a carbonium ion may, therefore, be associated with two successive stages: elimination of a proton from complex ion, $[H_2F]^+$, $[H_3SO_4]^+$, or $[H_4PO_4]^+$, and its addition to a double bond. The tendency for protons to be eliminated is not identical for different ions and may not be related to the conductivity.

The catalytic activity is most fully expressed by Hammett's function [3], which is determined with the aid of indicators and characterizes the tendency for an acid catalyst to lose a proton when a proton acceptor appears. Since this method is associated with the use of colored indicators, it is suitable only for uncolored media.

In the present investigation we have studied the conductivity of a number of acid catalysts in relation to their catalytic activities, and we have studied also the variation of conductivity in the course of alkylation and polymerization reactions. Apart from the usual alkylation and polymerization catalysts, the compounds of boron trifluoride, which comprise a large group of catalysts, are of great interest. The most interesting of these are the strong complex acids, such as $BF_3 \cdot H_2O$; $BF_3 \cdot 2H_2O$; $HF \cdot H_2O \cdot BF_3$; $H_3PO_4 \cdot BF_3$.

A number of papers has appeared recently on the electrochemistry of boron trifluoride compounds. The material published on this question is, however, very limited in scope, and is concerned with only a few compounds. Thus, up to 1950 the conductivity was known for only five boron trifluoride compounds [4]:

Compound	Conductivity at 25°	
$(C_2H_5)O \cdot BF_3$	$\kappa = 2.97 \cdot 10^{-4}$ ohm$^{-1}\cdot$cm^{-1}	[4]
$BF_3 \cdot H_2O$	$\kappa = 42.0 \cdot 10^{-3}$ ohm$^{-1}\cdot$cm^{-1}	[4]
$BF_3 \cdot 2H_2O$	$\kappa = 105.0 \cdot 10^{-3}$ ohm$^{-1}\cdot$cm^{-1}	[5]
$BF_3 \cdot 2CH_3OH$	$\kappa = 22 \cdot 10^{-3}$ ohm$^{-1}\cdot$cm^{-1}	[4]
$BF_3 \cdot 2C_6H_5OH$	$\kappa = 1.1 \cdot 10^{-3}$ ohm$^{-1}\cdot$cm^{-1}	[6]
BF_3 liquid at −120°	$\kappa = 5 \cdot 10^{-13}$ ohm$^{-1}\cdot$cm^{-1}	[7]

The conductivity of the etherate of boron trifluoride has been investigated over the range −9.4° to +44.7° [4], its extreme values being $1.344 \cdot 10^{-4}$ and $4.58 \cdot 10^{-4}$ ohm$^{-1}\cdot$cm^{-1} respectively. The conductivity of boron trifluoride dihydrate $BF_3 \cdot 2H_2O$ varies from $4.81 \cdot 10^{-2}$ to $10.52 \cdot 10^{-2}$ ohm$^{-1}\cdot$cm^{-1} over the range + 2.6 −45.5° [8]. Conductivity varies linearly with temperature.

A paper has been published recently by Sklyarenko [9] on the determination of the conductivity and other physicochemical properties of orthophosphoric acid at various concentrations at 25°.

Concentration of H_3PO_4 (%)	Density (g/cc)	Specific conductivity (ohm$^{-1}\cdot$cm^{-1})
81.39	2.6401	0.09916
88.22	1.7242	0.07466
93.10	1.7886	0.06150
97.35	1.8443	0.05093

For sulfuric acid at concentrations of 80, 90, and 100% at 18°, conductivity values of 0.119, 0.107, and 0.0157 ohm$^{-1}\cdot$cm^{-1} respectively are cited.

The investigation of the conductivity of a few BF_3 compounds has made it possible to elucidate the structure of boron trifluoride compounds [10]. Thus, the high conductivity of boron trifluoride hydrates shows that they are strong acids of the type of trifluorhydroxyboric acid $H^+[HO:BF_3]$ and the hydrate of this acid $H_3O^+[HO:BF_3]$. The ethyl-etherate of boron trifluoride has a considerably greater conductivity ($2.97 \cdot 10^{-4}$ ohm$^{-1}\cdot$cm^{-1}) than those of the original ether ($3 \cdot 10^{-13}$ ohm$^{-1}\cdot$cm^{-1}) and liquid BF_3 ($5 \cdot 10^{-13}$ ohm$^{-1}\cdot$cm^{-1}), thus indicating the appreciable ionization of the etherate molecule. Electrolysis of the ethyl-etherate is accompanied by evolution of hydrogen and ethane. On this basis we can regard the etherate of boron trifluoride as an ethyl derivative of trifluoroethoxyboric acid $C_2H_5^+[C_2H_5O:BF_3]$, the ionization of which is less marked than that of the acid itself [4].

EXPERIMENTAL

The conductivity of the acid catalysts was determined by the usual method with an apparatus consisting of an alternating-current sound generator GZ-1, a resistance box R-14, a drum slide wire, and a vessel containing platinum electrodes. In determining the conductivity, the catalyst (5-6 ml) was placed in a beaker, which was kept in a thermostat to acquire the required temperature. The platinum electrodes were then lowered into the electrolyte, and the conductivity was measured. Several determinations of the conductance were made, and on the basis of these the specific conductivity was calculated by the formula $\kappa = c \cdot k$, in which c is the cell constant and k is the conductance. Below we give the conductivities of a number of acid catalysts, according to the authors' determinations, and also information on the catalytic activity of the catalysts in alkylation and polymerization reactions.

Although acid catalysts are not completely chemically pure substances, since they cannot be distilled or purified by known methods, different samples of the same catalyst prepared at different times were found to have conductivities of the same order. In Table 1 a systematic scheme is given showing the activities and conductivities of a number of catalysts.

TABLE 1

Conductivities and Activities of some Catalysts*

No.	Catalyst	Conductivity at 25° ($ohm^{-1} \cdot cm^{-1}$)			Alkylation of isobutane, isopentane, olefins**			Polymerization at atm. press. and 100°**		
		specific	equiv.	molar	C_2H_4	C_3H_6	C_4H_8	C_2H_4	C_3H_6	i-C_4H_8
1	HF	–	–	–	0	+	+	0	+	+
2	$H_3PO_4 \cdot BF_3$	0.00722	0.205	0.615	+	+	+	Weak	+	+
3	$H_4P_2O_7 \cdot 2BF_3$	0.0067	0.270	1.080	+	+	+	Weak	+	+
4	$BF_3 \cdot H_2O$	0.0386	0.940	1.880	+	+	+	–	+	+
5	$BF_3 \cdot 2H_2O$	0.1660	–	–	0	0	0	0	0	+
6	$CH_3OH \cdot BF_3$	0.01371	0.966	–	0	Weak	+	–	–	–
7	$C_2H_5OH \cdot BF_3$	0.00854	0.718	–	0	Weak	+	0	–	–
8	$C_4H_9OH \cdot BF_3$	0.00053	–	–	0	0	0	0	+	+
9	$(C_2H_5)_2O \cdot BF_3$	0.0003	–	–	0	0	0	0	0	+
10	$H_2SO_4 + BF_3$	0.03569	–	–	+	+	+	–	+	+
11	H_2SO_4	0.03569	1.158	2.316	0	Weak	+	0	Weak	+
12	H_3PO_4	0.0510	0.885	2.66	0	0	0	0	0	+

* The preparation of the catalysts and their properties are given elsewhere [10, 11].

** The sign + indicates that the reaction goes, and the sign 0 indicates that it does not.

No general relation is to be observed between conductivity and catalytic activity. Strong acids, which are active catalysts, have in a number of cases a lower conductivity than less active catalysts.

We give below a table showing the variation of conductivity with temperature for some of the principal catalysts.

TABLE 2

Variation of Conductivity with Temperature

Temperature (°C)	Specific conductivity ($ohm^{-1} \cdot cm^{-1}$)			
	H_2SO_4 (100.1%)	H_2SO_4 (100.1%) + BF_3	$H_3PO_4 \cdot BF_3$	H_3PO_4
0	–	–	0.003207	–
5	0.022005	0.017147	0.004357	–
10	0.029177	0.020119	0.004592	–
15	–	0.025250	0.005209	–
20	0.033685	0.027058	0.005834	–
25	0.043595	0.035694	0.007227	0.0510
30	0.049742	0.041639	0.008108	–

Conductivity varies linearly with temperature (Fig. 1).

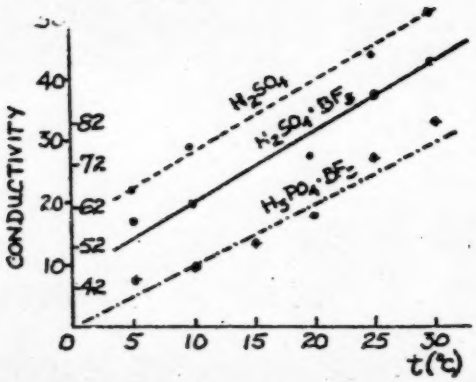

Fig. 1. Variation of conductivity of catalysts with temperature.

A study was made of the variation of the conductivity during polymerization and alkylation reactions. For these reactions we took chemically pure benzene, isopentane, and olefins (propene and 2-methylpropene), which were prepared by the dehydration of the corresponding alcohols (olefin content of the gas 98-99%). A number of successive experiments were carried out, and after each of these we determined the yield of polymers or alkyl derivative, the density, conductivity, and catalyst concentration.

Variation in Conductivity in the Alkylation of Benzene with Propene. Successive experiments were carried out on the alkylation of benzene with propene at 15° and atmospheric pressure. For each experiment we took 200 ml of benzene, 30.5 liters of propene (molar ratio 2.75:1), and 25 ml of catalyst, which took part in a number of successive experiments.

After each experiment the reaction product, which consisted of isopropyl benzene (b.p. about 152°) and polyisopropylbenzenes, was fractionated, and the yield of alkyl derivatives boiling above 120° was determined on the basis of the propene taken. The alkylation procedure has already been given in detail by the authors [11]. The results of the experiments are given in Table 3.

TABLE 3

Variation of yield, consumption and properties of $H_3PO_4 \cdot BF_3$ catalyst in the alkylation of propylbenzenes

No.	Yield of alkyl deriv. based on propene (b.p. above 120°)	Catalyst consumption (% on alkyl deriv. obtained)	Sp. gr. of catalyst	Spec. conductivity at 25° ($ohm^{-1} \cdot cm^{-1}$)
0	–	–	1.900	0.00722
1	186	46.2	1.823	0.00647
2	220	21.4	1.816	0.00624
3	236	13.9	1.812	0.00618
4	260	2.9	1.625	0.00535
5	130	8.5	1.331	0.00058

During the reaction the catalyst concentration falls as a result of the dissolution of unsaturated hydrocarbons, and this is shown by a fall in specific gravity and conductivity. At a certain point the activity of the catalyst falls sharply (the yield falls), and this point corresponds to a sharp fall in the conductivity and specific gravity of the catalyst. The graph in Fig. 2 shows the variation in the specific conductivity of the catalyst in the course of reactions carried out in a series of successive experiments with one portion of catalyst.

Variation in Conductivity in the Alkylation of Isopentane with 2-Methylpropene. The alkylation of isopentane with 2-methylpropene was carried out in presence of 98.5% sulfuric acid. 2-Methylpropene (5 liters) was passed into a vigorously agitated mixture of 50 ml of isopentane and 30 ml of sulfuric acid at 10°. The hydrocarbon layer was then distilled, yielding alkyl derivatives boiling in the range 30-170° and a residue boiling above 170°. The results of the experiments are given in Table 4.

Change in the catalyst activity during the alkylation reaction is accompanied by change in conductivity, and the conductivity of the catalyst can, therefore, serve as a supplementary characteristic of the alkylation process.

Conductivity of Sulfuric Acid in the Polymerization of Propene and 2-Methylpropene. Alkylation is always accompanied to some extent by polymerization, and in a number of cases polymerization can be considered as an independent process, so that the study of the conductivity of catalysts in relation to the polymerization process is of undoubted interest.

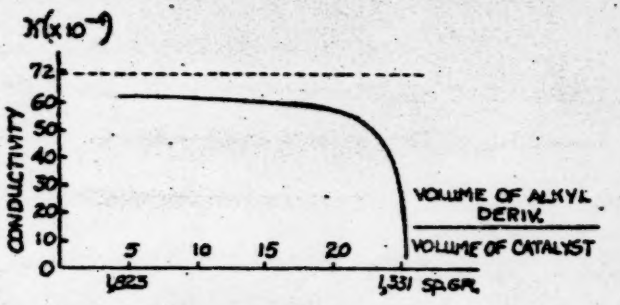

Fig. 2. Variation of conductivity of catalyst in the course of reaction.

TABLE 4

Variation of Yield, and of the Consumption and Properties of Sulfuric Acid, for the Alkylation of Isopentane with 2-Methylpropene*

Expt. No.	Yield of alkyl derivative (% on 2-methylpropene)		Sp. gr. of alkyl deriv. d_4^{20}	Consumption of catalyst (% on alkyl derivative)	Sp. gr. of acid d_4^{20}	Concentration of acid (%)	Specific conductivity at 25° ($ohm^{-1} \cdot cm^{-1}$)
	at 30-170°	above 170°					
0	–	–	–	0	1.842	98.3	0.1150
3	183	28	0.708	209	1.766	90.0	0.1000
4	162	58	0.710	85.5	1.734	86.9	0.0930
6	82	82	0.729	83.7	1.690	83.0	0.0674
7	20	105	0.746	53.2	1.525	62.6	0.0341
8	12.5	42	0.760	51	1.4190	60.6	0.0233

* The authors have already given details of the procedure [11].

The polymerization of olefins in presence of H_2SO_4 and $H_3PO_4 \cdot BF_3$ was carried out in a solvent, namely heptane. Propene or 2-methylpropene was passed into a vigorously agitated emulsion of the catalyst and solvent. The

reaction was carried out at 20-25°, the rate of passage of gas being 1-1.5 liter/hour. After each experiment, in the course of which 4-5 liters of gas was passed, the hydrocarbon layer was separated from the acid layer, washed, and dried. The heptane (b.p. 98.4°) was distilled off up to a temperature of 100°, since the polymers obtained under these conditions boil above 100°. After each experiment the conductivity, titratable acidity, and specific gravity of the catalyst were determined. The polymers were not specially investigated, since this question has been examined in previous investigations [11].

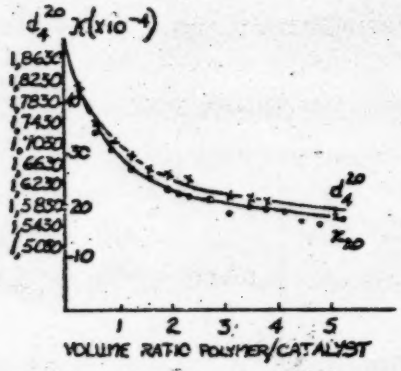

Fig. 3. Variation of conductivity and specific gravity in the polymerization of 2-methylpropene.

The polymerization of propene in presence of sulfuric acid did not proceed very rapidly: a large part of the propene dissolved in the acid, leading to rapid increase in the volume of the acid layer, fall in the acid concentration, and fall in its conductivity, so that polymerization ceased. Under similar conditions 2-methylpropene polymerized readily, and the concentration and conductivity of the acid fell only slowly: over a series of experiments the yield did not change appreciably. The results of the experiments are given in Table 5.

In Fig. 3 a comparison is made of the variations of the conductivity of the catalyst H_2SO_4 in the polymerization of propene and 2-methylpropene, and in the alkylation of 2-methylpropene. In the course of polymerization the electrochemical properties of the catalyst change greatly, but in the course of alkylation the change in the catalyst is slow. Introduction of a substance capable of being alkylated into the reaction raises the stability of sulfuric acid when it reacts with olefins. A polymerization side reaction during alkylation will, therefore, encourage poisoning of the catalyst.

TABLE 5

Variation in the Properties of an H_2SO_4 Catalyst during the Polymerization of Propene and 2-Methylpropene

Expt. No.	Yield of polymer (%)	Sp. gr. of polymer d_4^{20}	Catalyst			Change in conductivity ($ohm^{-1} \cdot cm^{-1}$)
			Consumption (%)	Sp. gr. d_4^{20}	Concentration (%)	
			Propene			
0	—	—	—	1.8351	93.5	0.10773
1	20.8	0.7450	3200	—	—	0.08644
2	15.0	0.7533	1835	1.6393	—	0.05823
4	11.4	0.7644	1106	1.3500	60.9	0.01620
6	4.2	0.7688	890	1.3327	40.3	0.00411
8	Traces	—	—	1.2700	20.4	0.00148
			2-Methylpropene			
1	83.6	0.7460	2100	1.8039	92.0	0.09802
2	66.4	0.7464	654.1	1.7180	86.1	0.07694
5	65.8	0.7852	341.1	1.6254	78.4	0.05358
7	66.4	0.7926	222.4	1.5554	68.9	0.03559
9	95.4	0.7734	154.7	1.5156	67.6	0.02506
10	74.3	0.8012	104.1	1.4220	60.1	0.01920

The compound of boron trifluoride with orthophosphoric acid is one of the most active polymerization catalysts known. We have studied the variation in its conductivity in the course of the polymerization of propene and 2-methylpropene. The experimental conditions were similar to those of the preceding experiment: 30 ml of catalyst, composition $H_3PO_4 \cdot BF_3$ (sp.gr. 1.906), was taken.

2-Methylpropene was found to polymerize very readily in presence of the complex formed by orthophosphoric acid with boron trifluoride, and the yield of polymer, therefore, remained practically unchanged during 15 successive experiments. Also, in the polymerization of propene, the catalyst remained active up to the end of the series of experiments.

TABLE 6

Variation in the Properties of a $H_3PO_4 \cdot BF_3$ Catalyst during the Polymerization of Propene and 2-Methylpropene

Expt. No.	Yield of polymer (%)	Sp. gr. of polymer d_4^{20}	Catalyst: Consumption (%)	Catalyst: Sp. gr.	Change in conductivity ($ohm^{-1} \cdot cm^{-1}$)
			Propene		
0	–	–	–	1.903	0.00520
2	81.3	0.7870	728	1.8201	0.00450
4	81.5	0.7951	360	1.7884	0.00421
6	95.0	0.7844	241	1.7831	0.00403
8	70.4	0.7824	187	1.7020	0.00240
			2-Methylpropene		
1	62.9	0.8119	866.7	1.8118	0.00427
2	74.6	0.8001	418.6	1.7464	0.00345
4	89.5	0.8050	190.0	1.6781	0.00273
7	95	0.8010	99.2	1.6361	0.00218
11	85.6	0.8156	61.1	1.5897	0.00197
15	70.1	0.8374	45.6	1.5641	0.00189

An interesting picture is presented when a comparison is made of the variations in the conductivity of the catalyst $H_3PO_4 \cdot BF_3$ in the polymerization of propene and 2-methylpropene and the alkylation of benzene (see Fig. 4). This picture is similar to that observed for sulfuric acid: the catalyst changes little during polymerization, although it is one of the most active polymerization catalysts.

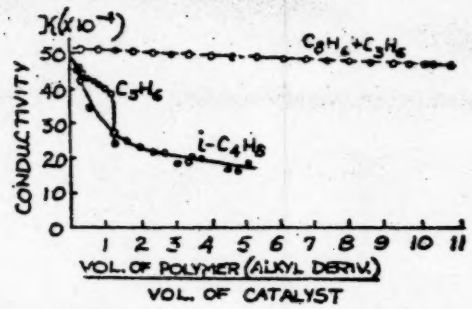

Fig. 4. Variation of the conductivity of $H_3PO_4 \cdot BF_3$ in alkylation and polymerization processes.

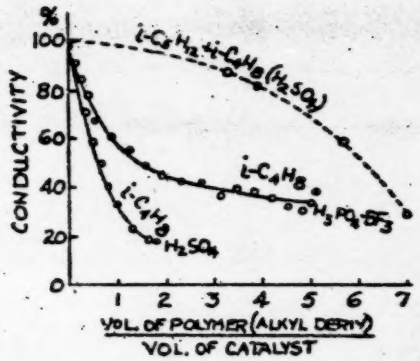

Fig. 5. Variation of the conductivity of catalysts during polymerization and alkylation.

Fig. 5 shows the variation of the conductivity (as percentage of initial value) of sulfuric acid and the complex of orthophosphoric acid with boron trifluoride in the course of the polymerization of 2-methylpropene and of the alkylation of isopentane with 2-methylpropene. The most marked change in conductivity in the course of reaction is observed for sulfuric acid. The conductivity of the catalysts changes rapdily during polymerization, and slowly during alkylation.

The lowering of the catalytic activity and conductivity of catalysts during the polymerization and alkylation of hydrocarbons is to be explained by the formation in the catalyst of partial and full esters, which have low conductivity and do not facilitate ionization. There is, consequently, a reduction in the concentration of the principal substance responsible for the conduction of the current and the promotion of catalysis. For this reason a definite relationship is to be observed between the degree of catalysis and the value of the conductivity, so long as no water is allowed to enter the reaction mixture.

SUMMARY

1. The conductivities of a number of acid catalysts have been investigated, tabulated, and compared with the catalytic activities of these substances.

2. No general relationship is to be observed between the catalytic activity and conductivity when a number of different catalysts are considered, but when one particular catalyst is under consideration, the conductivity forms an index of the activity of the catalyst. The conductivity falls parallel to the specific gravity and titratable concentration of the catalyst.

3. Comparison of conductivities in polymerization and alkylation reactions shows that in alkylation the conductivity changes very slowly, whereas in polymerization it changes very rapidly. Although the alkylation reaction occurs in presence of strong acids and, in general, with a smaller group of catalysts than the polymerization reaction, the stability of the catalyst is considerably higher in alkylation than in polymerization.

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STUDY OF THE EFFECT OF PRESSURE ON THE POLYCONDENSATION OF THE METHYL ESTER OF GLYCINE

A. M. Polyakova, L. F. Vereshchagin, A. A. Sakharova, and E. S. Tambovtseva

The present investigation forms a continuation of the work of Polyakova and Vereshchagin on the effect of pressure on the hydrolysis of 2,5-piperazinedione and the formation of polypeptide linkages [1]. The authors showed that increase of pressure greatly increases the rate of hydrolysis of 2,5-piperazinedione. Also, it was found that the final reaction mixture consisted not only of liquid hydrolyzate, but contained also a solid water-insoluble product. It was considered that the solid compound was a polypeptide formed from residues of hydrolyzed 2,5-piperazinedione.

Increase in pressure, therefore, not only leads to increase in the rate of hydrolysis of 2,5-piperazinedione, but also results in the formation of polypeptides from the amino acid molecules produced in the hydrolysis. The authors of this paper did not, however, succeed in determining the mean molecular weight of the solid compound, owing to its extremely low solubility.

The question of the effect of pressure on the rate of formation of polypeptides from amino acids and their esters is undoubtedly of great theoretical and practical interest. In view of this fact we have, in the present work, undertaken a study of the behavior of esters of amino acids under pressure. The reason for the choice of esters of amino acids as monomers is that the resulting alkoxyl end groups permit the number of units in the polymer chain formed to be determined comparatively readily, even when the polymer is insoluble in the usual organic solvents.

The simplest of the amino acid esters, the methyl ester of glycine, was selected for investigation. As early as 1888 Curtius [2], who was the first to obtain the methyl ester of glycine in the free state, found that, when this ester was left for a few days in a sealed tube, it was converted into a white solid mass. This phenomenon was given the name "polymerization", but its essential character was not discovered by Curtius. Later, in 1904 [3], the same worker showed that in the polymerization of the ethyl ester of glycine under like conditions a tetraglycyl compound was formed, namely $NH_2CH_2CO(NHCH_2CO)_2NHCH_2CO_2C_2H_5$, which was called a "biuret base" by the author. Curtius showed that, apart from the tetraglycyl compound, glycine anhydride was always present in the polymerization products. The next work on the polymerization of glycine esters appeared in 1939.

In a short communication Frankel and Katchalski [4] gave their experimental results on the polycondensation of the ethyl ester of glycine. The authors, who did not draw any theoretical conclusions, showed that by variation of the medium and temperature conditions, and by passage of gas through the ester, linear polymers of 12 to 20 units could be obtained. All of the polymers obtained were homlike in nature and were practically insoluble in hot water. The question of the polycondensation of glycine esters is treated in greater detail in a paper by the same authors, which appeared in 1942 [5]. The data supplied by this paper concerning the polycondensation of the methyl, ethyl, and isobutyl esters of glycine are mutally complementary. The authors showed that the methyl ester of glycine, when left in an open vessel for one month, yields a fraction that is insoluble in hot water and contains 18 amino acid residues. Also, when nitrogen is passed for 12 hours and the reaction mixture is set aside for one month at room temperature, a polymer of 30 units is obtained. When the methyl ester of glycine is kept in dry ether for three months at room temperature, a polymer of 27 units can be obtained, and when the ester is boiled in dry toluene for four hours and the reaction mixture is then left for three months, a polymer containing 35 monomer units is obtained.

Frankel and Katchalski consider that the glycine ester polymers that they isolated have a straight chain structure, this contention being proved, in their opinion, by the following facts, which they have established: 1) the proved presence of alkoxyl and amino end groups; 2) the obtaining of the biuret reaction during the alkaline hydrolysis of polymer molecules; 3) the quantitative agreement between the number of glycine residues in the condensation product (calculated from the content of alkoxyl groups) and the number of amino acid molecules liberated in the complete acid hydrolysis of the condensed molecules.

The paper of Fraenkel-Conrat et. al. [6], which appeared in 1945 and was concerned with questions relating to the preparation of polyglycine esters, contains no data that are essentially different from those that we have cited. The authors kept the methyl ester of glycine in ether solution at room temperature for one month, and obtained, in addition to low polymers, highly polymeric glycine esters containing 15 glycine units. In confirmation of this value

of the chain length, the authors give analytical figures for free amino nitrogen, amino nitrogen liberated by acid hydrolysis, and bound nitrogen.

It was considered to be of interest to study the polycondensation of the methyl glycine ester under super-high pressures at various temperatures. Also, it was considered to be important to establish the structure of the polymers with certainty, for the proof given by Katchalski of the linear-chain structure is not convincing: all of the arguments given above will apply also if there are cyclic groupings in the molecule, for example 2,5-piperazinedione units.

It must be noted that according to the 2,5-piperazinedione theory, which was advanced by Zelinsky in 1914 and developed by him, in conjunction with Sadikov in 1923 [7], the protein molecule, which is a polymer formed from amino acids, is bound to contain not only polypeptide chains, but also 2,5-piperazinedione rings. The researches of Zelinsky, Gavrilov, and coworkers have shown the readiness with which 2,5-piperazinediones are destroyed, and also the possibility of the formation of 2,5-piperazinedione rings under the conditions employed for the hydrolysis of proteins with the object of determining their structure.

Gavrilov and Koperina [8] have proposed a method of electrolytic reduction which, unlike previous methods for the determination of piperazinediones, permits the presence and number of piperazinedione rings in the protein molecule to be established with exactness. We have taken this method as our basis in proving the structure of polymers of glycine methyl ester formed under conditions of normal and super-high pressures.

In the present investigation we have studied the polycondensation of glycine methyl ether at 4500 atm and at various temperatures (room, 50, 75, and 130°). At the same time, comparative experiments were carried out at atmospheric pressure. As a result of the reaction a mixture of polycondensation products was obtained, from which we separated only the macromolecular polymers, insoluble in hot water. Investigation of the reaction products showed that high pressure results in increased rate of reaction and in the degree of polycondensation. In order to decide the question of the structure of the polymers obtained, we subjected them to electrolytic reduction by Gavrilov and Koperina's method.

Our tests showed that our polymers would not undergo the electrolytic reduction reaction that was to be expected if piperazinedione rings were present in the polymer molecule. This gave us reason to suppose that linear-chain molecules may be formed when polycondensation occurs under high-pressure conditions. Calculations of the theoretical contents of amino nitrogen and methoxyl groups based on a linear-chain structure for the polycondensation products were in good agreement with the experimental results. Since the polymers obtained were insoluble in all of the organic solvents that we tried, we could determine the molecular weight (and so the number of mononer units in the polymer) only by the chemical method: by the content of methoxyl end groups. We determined the methoxyl content by Viebŏck's method, and the analytical results were confirmed by hydrolysis followed by determination of amino nitrogen by titration according to the methods of Sorensen and Linderstrŏm-Lang, and also by the preparation of copper salts.

EXPERIMENTAL

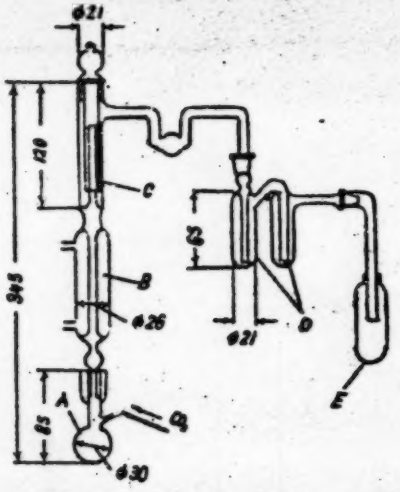
Preparation of Starting Materials. The methyl ester of glycine was prepared by the method proposed by Frankel and Katchalski in which the hydrochloride of glycine methyl ester is suspended in absolute ether and decomposed by a current of dry ammonia at 0°; it had the following constants: b.p. 46.5° (12 mm); 48.5° (16 mm); 54° (20 mm). For glycine methyl ester the literature gives: b.p. 45° (20 mm) [5]; b.p. 130° (760 mm) [6]; 54° (50 mm), average yield 48.4% [2]. In its turn the hydrochloride of glycine methyl ester was prepared by the following series of reactions: glycine $\xrightarrow{HCl}$ glycine hydrochloride $\xrightarrow{HCl,\ CH_3OH}$ hydrochloride of glycine methyl ester, m.p. 174.5-175° (the literature [2] gives 175°).

Found %:	C 28.73; 28.94;	H 6.62; 6.59;	N 11.44; 11.32
$C_3H_6O_2NCl$. Calculated %:	C 28.69	H 6.42	N 11.16

Experimental Procedure. The experiments on polycondensation under pressure were carried out in a strong tube of plastic material, length 10 cm, internal diameter 6.5 mm, wall thickness 2.5 mm. The ends of the tube were provided with pistons, by means of which the pressure was communicated to the substance under investigation; the tube was encased in copper. It was placed in a high-pressure reactor filled with freshly distilled, anhydrous glycerol. The reactor was immersed in an oil bath provided with electric heater, stirrer, and contact and control thermometers. The pressure was applied by means of a hydraulic compressor. The variation from the stipulated experimental temperatures did not exceed $\pm$ 1°.

The routine was the same for all of the pressure experiments; it was as follows: For the first 18 hours the glycine methyl ester was under pressure at room temperature. Heat was then applied for six hours (pressure experiments

were carried out at elevated temperature), and 18 hours after heating ceased the pressure was released. Hence, the glycine methyl ester was under pressure for 42 hours altogether, and this period included six hours during which heat was applied.



Apparatus for the quantitative determination of methoxyl content: A) reaction vessel; B) condenser; C) column containing a suspension of red phosphorus in water; D) absorption vessel containing a mixture of sodium acetate, acetic acid, and bromine; E) absorption vessel containing a mixture of sodium acetate and formic acid.

The polycondensation reaction carried out at the same temperatures, but under atmospheric pressure, was performed in glass tubes protected by soda-lime tubes and immersed in an oil thermostat. As in the pressure experiments, the reaction proceeded for 18 hours at room temperature, heating was then applied for six hours, and after a further 18 hours at room temperature the experiment was concluded. The routine in the experiments at high pressure and at atmospheric pressure was therefore the same.

Treatment of the Reaction Products

The product obtained as a result of the polymerization was transferred to a weighed tube for centrifugation, and was washed in the centrifuge with hot water until the washings showed a negative reaction with picric acid (absence of 2,5-piperazinedione) and a negative biuret reaction (absence of low polymers, soluble in water). The water-insoluble polymerization product was dried in a vacuum desiccator. When constant weight was attained, the electrolytic reduction of the product was carried out, the methoxyl content was determined, and the product was hydrolyzed with 25% hydrochloric acid and then determined as the copper salt of glycine.

Determination of Cyclic Groupings in the Polymers by the Electrolytic-reduction Method. The electrolytic reduction of the product was carried out by the method of Gavrilov and Koperine [8]. In the hydrolyzates obtained before and after reduction, the total nitrogen was determined by the Kjeldahl method and the amine nitrogen by Sörensen's method, as modified by Gavrilov. The results of the electrolytic reduction of the product obtained by the polycondensation of glycine methyl ester at 4500 atm and 75° are presented in Table 1.

TABLE 1
Analysis for Nitrogen in Different Forms, Before and After Reduction

Conditions of experiment	Total N in solution (g)	Amino N	
		(g)	(% of total N)
Before reduction after hydrolysis	0.0474	0.0485	102.32
After reduction after hydrolysis	0.0376	0.0380	101.06

As will be seen from Table 1, no reduction in the amount of nitrogen titratable by Sorensen's method in the hydrolyzate of the product obtained after electrolytic reduction is observed, which may be taken as a proof of the absence of 2,5-piperazinedione rings.

TABLE 2
Quantitative Determination of the Methoxyl Content by Viebock's Method

Conditions under which product obtained		CH_3O content (%)
Pressure (atm)	Temperature (°C)	
1	75°	2.16
4500	50	0.71
4500	75	0.80
4500	130	0.95

We determined the methoxyl content by Viebock's method [9].

In the course of the work we introduced some slight modifications in the apparatus (see figure). Also, instead of the recommended hydriodic acid of sp.gr. 1.7, we used acid of sp.gr. 1.96. The analytical results are given in Table 2.

The hydrolysis of the product for amino nitrogen determination was carried out with 25% hydrochloric acid at the boil for six hours. The hydrolyzate was

TABLE 3

Quantitative Determination of Amino Nitrogen by Titration by the Methods of Linderstrom-Lang and Sorensen, and of Total Nitrogen by the Kjeldahl Method

Substance	Amino N calculated theoretically from methoxyl content (%)	Experimental value of amino N (%)		Total N by Kjeldahl
		by Linderstrom-Lang	by Sorensen-Gavrilov	
Glycine	18.66	18.72	–	–
Glycine	18.66	18.75	–	–
Glycine	18.66	18.50	–	–
Product obtained at 75° and 4500 atm	24.35	23.90	24.29	23.91

TABLE 4

Quantitative Determination of the Copper Salt

Conditions under which product obtained		Amount of copper salt		Amount of copper oxide	
Pressure (atm)	Temperature (°C)	Calculated theoretically from methoxyl content (g)	Obtained theoretically (g)	Calculated (g)	Found (g)
4500	75	0.1377	0.1338	0.0065	0.0064
4500	75	0.1373	0.1363	0.0049	0.0050

TABLE 5

Effect of Pressure and Temperature on the Rate of the Polycondensation of Glycine Methyl Ester and on the Mean Molecular Weight of the Product

Pressure (atm)	Temperature (°C)	Methoxyl content (%)	Mean no. of groups	Mean molecular weight	Yield (%)
1	Room	No Product Obtained			
1	50	Traces of Product			
1	75	2.16	25	1458	4.08
4500	Room	No Product Obtained			
4500	50	0.71	76	4368	10.61
4500	75	0.80	67	3855	13.04
4500	130	0.95	57	3284	18.91

neutralized with caustic soda solution, and the amino nitrogen was determined by titration, following Sorensen and Linderstrom-Lang [10]. This procedure was first checked with glycine. The product obtained at 75° and 4500 atm was analyzed in this way (Table 3).

The quantitative determination of the copper salt was carried out by Heintz's method [11], and for this purpose the product was hydrolyzed with 10% sulfuric acid at the boil (Table 4).

As will be seen from the tables, the results for the amino-nitrogen and copper salt estimations were is good agreement with the methoxyl-determination results.

Discussion of Results. In Table 5 we give data showing the dependence of the rate of polycondensation of glycine methyl ester and the mean molecular weight of the product on pressure and temperature.

It will be seen from Table 5 that at 50° and atmospheric pressure only traces of macromolecular polypeptides are obtained, and it was not found possible to analyze these owing to the small amount formed. At 4500 atm, however, at the same temperature, a mixture of macromolecular polypeptides was obtained in 10% yield, and the methoxyl content, 0.7%, corresponded to an average of 76 monomer units per molecule, if we assume the polypeptides formed to be of linear structure. In the experiments at 75° and atmospheric pressure, a mixture of water-insoluble polypeptides was obtained in 4.08% yield, and the methoxyl content, 2.16%, corresponded to a mean chain length of 25 monomer units. At 4500 atm and at the same temperature, the yield of macromolecular polypeptides was 13%, and the methoxyl content was 0.80%, corresponding to an average of 67 monomer units per molecule.

These experiments show also the effect of temperature on the course of the polycondensation of the glycine ester under pressure. As Table 5 shows, no macromolecular reaction products are formed at room temperature. At 50° and 75° the effect of rise of temperature on the reaction rate and degree of polymerization is seen, but with further rise in temperature to 130°, only the yield of macromolecular polypeptides increases.

We thus see the effect of pressure on the rate of polycondensation and on the mean molecular weight of the product at the temperatures 50°, 75°, and 130°. At 75°, for example, both the yield of macromolecular polypeptides obtained as a result of the polycondensation reaction and the mean molecular weight of these products are approximately three times as great at 4500 atm as at atmospheric pressure.

SUMMARY

1. The polycondensation of glycine methyl ester has been investigated at a pressure of 4500 atm and at various temperatures (room, 50°, 75°, 130°).

2. It has been established that high pressure increases the rate and extent of the polycondensation of glycine methyl ester.

3. The effect of temperature on the polycondensation of glycine methyl ester under pressure has been determined.

4. An attempt has been made to determine the structure of the products of the polycondensation under pressure of glycine methyl ester.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 11. BEHAVIOR OF 2-METHYL-2-BUTENE AND 2,3-DIMETHYL-2-BUTENE IN THE CATALYTIC HYDROCONDENSATION REACTION

Ya. T. Eidus, K. V. Puzitsky, and A. P. Meshcheryakov

The catalytic hydrocondensation of carbon monoxide with olefins has been now effected with ethylene and its closest homologs, the α-olefins [1]. Experiments with the object of extending the reaction to 2-methylpropene [2] showed that this unsymmetrical dimethylethylene readily enters into hydrocondensation with carbon monoxide, and that the active part of the molecule is the unsubstituted methylene group. This is evident from the fact that the reaction products consist essentially of hydrocarbons having a methyl side group on the second carbon atom.

The present investigation had the object of studying the behavior of tri- and tetra-substituted ethylenes, i.e., 2-methyl-2-butene and 2,3-dimethyl-2-butene, in the reaction of hydrocondensation with carbon monoxide. It is of interest to note that according to the literature [3] these two hydrocarbons do not enter directly into the catalytic oxo-synthesis reaction, i.e., into the reaction leading to the synthesis of alcohols from olefins, carbon monoxide, and hydrogen under pressure. Under the conditions of this synthesis 2-methyl- and 2,3-dimethyl-2-butenes are first isomerized to α-olefins, which then enter into the oxo-synthesis reaction with formation of the corresponding alcohols.

EXPERIMENTAL

Synthesis of 2-Methyl-2-butene and 2,3-Dimethyl-2-Butene

For the synthesis of 2-methyl-2-butene, we used fermentation amyl alcohol, which was dehydrated over aluminum oxide at 450-500° to a mixture of 3-methyl-1-butene, 2-methyl-1-butene, and 2-methyl-2-butene. This mixture of pentene isomers was treated, following Vyshnegradsky [4, 5] with dilute sulfuric acid under ice cooling. The 3-methyl-1-butene, which remained in the upper layer, was separated, and the lower layer was diluted with water and hydrolyzed. The product was distilled twice, and the fraction of b.p. 37-38° was again distilled over sodium, yielding 85 ml of a fraction (2-methyl-2-butene), b.p. 37-38° at 753 mm. The 2-methyl-2-butene obtained comprised about 45% of the original mixture of pentene isomers, and it had the following constants: b.p. 37-38° (753 mm); d_4^{20} 0.6590; n_D^{20} 1.3860; Found MR 24.98; Calculated MR 24.82. The literature [6, 7] gives: b.p. 38.5-38.6° (760 mm); d_4^{20} 0.6620; 0.6596; n_D^{20} 1.3869; 1.3876.

We prepared 2,3-dimethyl-2-butene according to the scheme:

$$(CH_3)_3CCOCH_3 \xrightarrow{H_2} (CH_3)_3CCH(OH)CH_3 \xrightarrow{Al_2(SO_4)_3} (CH_3)_2C=C(CH_3)_2 + H_2O.$$

Pinacolyl alcohol was prepared by hydrogenation of pinacolone (b.p. 106°) in presence of a 30% Bag nickel catalyst [8], the initial hydrogen pressure being 80-100 atm and the temperature 160-180°. The pinacolyl alcohol obtained (220 ml) was fractionated, and the fraction of b.p. 118-120° at 757 mm (90%) was then dehydrated over anhydrous aluminum sulfate prepared by the method indicated above.

According to the literature [9], pinacolyl alcohol, and also the normal product of its dehydration, 3,3-dimethyl-1-butene, are converted in the vapor phase in presence of anhydrous aluminum sulfate at 275° into a mixture of products containing 62-63% of 2,3-dimethyl-2-butene, 33-34% of 2,3-dimethyl-1-butene, and 3.5-4.3% of 3,3-dimethyl-1-butene.

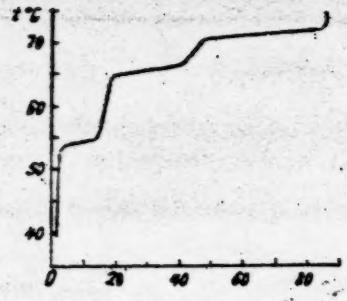

Fig. 1. Fractionation curve for the product of the dehydration of pinacolyl alcohol over aluminum sulfate.

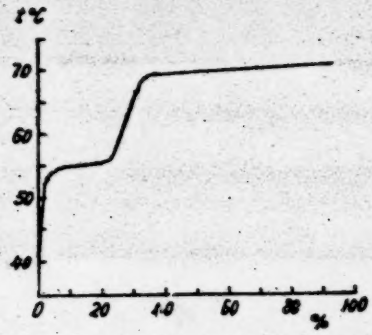

Fig. 2. Fractionation curve for the product of the dehydration of Fractions I-V (Table 1) over aluminum sulfate.

TABLE 1

Fraction No.	Boiling range (°C)	Amount (% by volume of original catalyzate)	d_4^{20}	n_D^{20}
I	40-54.5	5.2	0.6712	1.3881
II	54.5-57	9.6	0.6922	1.3920
III	57-66	5.9	0.6904	1.4038
IV	66-67	21.6	0.6933	1.4027
V	67-71	5.9	0.6987	1.4070
VI	71-73	37.7	0.7075	1.4128
Residue	—	7.4	—	—
Losses	—	6.7	—	—

From 200 ml of pinacolyl alcohol dehydrated for 27 hours at 275° over anhydrous aluminum sulfate, 170 ml of catalyzate and 20 ml of water were obtained. The catalyzate was separated from the water, washed, dried, and fractionated through a 40-plate column having a filling of single metal spirals. The volume of catalyzate taken for fractionation was 135 ml; the fractionation curve, obtained for a pressure of 744 mm, is given in Table 1.

Fraction VI (53 ml, b.p. 71-73°) had the constants d_4^{20} 0.7075 and n_D^{20} 1.4128, and consisted of 2,3-dimethyl-2-butene: Found MR 29.62; Calculated MR 29.44. For 2,3-dimethyl-2-butene the literature [6] gives: b.p. 73.2° at 760 mm; d_4^{20} 0.7086; n_D^{20} 1.4121.

Fractions I-V were united, and 54 ml was again passed at 275° for five hours over a fresh portion (75 ml) of anhydrous aluminum sulfate, yielding 51 ml of catalyzate, which was washed, dried, and fractionated (740 mm) as before. The curve for the fractionation of 43 ml is given in Fig. 2.

Two fractions were taken: Fraction I (17 ml), boiling range 41-70°, and Fraction II (22 ml), boiling range 70-71.6°, d_4^{20} 0.7086; n_D^{20} 1.4120. Fraction II, which consisted of 2,3-dimethyl-2-butene (Found MR 24.53; Calculated 24.44), was united with the corresponding fraction of the first catalyzate. In this way 75 ml of 2,3-dimethyl-2-butene was obtained and was used in the experiments on hydrocondensation with carbon monoxide. It may be noted that the low plateaus on the fractionation curves in Fig. 1 and 2 (b.p. 55-56°) correspond to 2,3-dimethyl-1-butene (the literature [6] gives b.p. 55.6°).

Experiments on the Hydrocondensation of Carbon Monoxide with 2-Methyl-2-butene and 2,3-Dimethyl-2-butene

The apparatus and procedure were the same as in the previous work on 2-methylpropene [2]. The experiments were carried out at 190° and atmospheric pressure in a continuous-flow system. The activity of the catalyst was checked beforehand in the hydrocondensation reaction of carbon monoxide with ethylene, and it was found to be high (yield of condensate 500 ml per cu. m at a space velocity of 100 liters/liter-hr.).

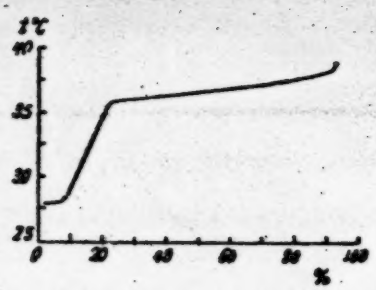

Fig. 3. Fractionation curve for the product of the hydrocondensation of carbon monoxide with 2-methyl-2-butene.

Experiments with 2-Methyl-2-butene. 2-Methyl-2-butene (85 ml, i.e., 0.8 mole) was passed from the buret to the reaction tube, which contained a 40-cm layer of Catalyst No. 52; a space velocity of 0.31 liter/liter·hr was maintained for nine hours. Simultaneously, a mixture of hydrogen and carbon monoxide was passed into the catalysis tube at a space velocity of 70 liters/liter·hr, the total amounts passing being 2.6 liters of CO and 24.5 liters of H_2. The gas-vapor phase had the following composition by volume: 39.7% 2-methyl-2-butene, 54.4% H_2, 5.9% CO. The liquid catalyzate obtained (75.0 ml) was dried with anhydrous copper sulfate and 51 ml of it was fractionated at 750 mm through the column described above. The fractionation curve is given in Fig. 3.

It will be seen from Fig. 3 that 93% by volume of the catalyzate distilled within the range 28-37.5°. The residue was distilled from a Favorsky flask over the range 55-240°. The fractions taken and their properties are given in Table 2.

It will be seen from Fig. 3 and Table 2 that 94% of the catalyzate consisted of C_5 hydrocarbons.

It would be expected that hydrogenation of 2-methyl-2-butene would yield 2-methylbutane (b.p. 27.9°, d_4^{20} 0.61972; n_D^{20} 1.3539 [6]). It can be seen from the properties of the condensate fractions obtained that Fractions I and II, comprising about 33% by volume, consist of 2-methylbutane contaminated with unchanged 2-methyl-2-butene, and Fractions III-IV, which comprise 60%, are essentially 2-methyl-2-butene. Fraction V can be considered as consisting of the products of hydrocondensation with carbon monoxide and the products of hydropolymerization, but it comprises only 5.9% by volume of the catalyzate. This fraction is mainly produced by the transformation of the original 2-methyl-2-butene, since not more than 0.5 ml of condensate can be obtained by synthesis from CO and H_2.

TABLE 2

Fraction No.	Boiling range (°C)	Amount (% by volume of original catalyzate)	d_4^{20}	n_D^{20}
I	28-29	11.8	0.6260	1.3635
II	29-36	21.5	0.6342	1.3780
III	36-37	23.5	0.6535	1.3832
IV	37.0-37.5	36.3	0.6585	1.3860
V	55-240	5.9	0.6729	1.3930

TABLE 3

Fraction No.	Boiling range (°C)	Amount (% by volume of original catalyzate)	d_4^{20}	n_D^{20}
I	28-30	3.8	–	1.3513
II	48-58	7.7	0.6555	1.3745
III	58	17.3	0.6626	1.3766
IV	58.5-63	19.2	0.6652	1.3794
V	63-71	18.5	0.6754	1.3988
VI	71-73	24.0	0.7096	1.4111
VII	80-137	11.5	0.7047	1.3989
Residue and losses	Above 137	3.0	–	–

It may therefore be regarded as established that, under the given conditions, only 5-6% of the 2-methyl-2-butene entered into the reaction of hydrocondensation with carbon monoxide, and 30-35% was hydrogenated to 2-methylbutane.

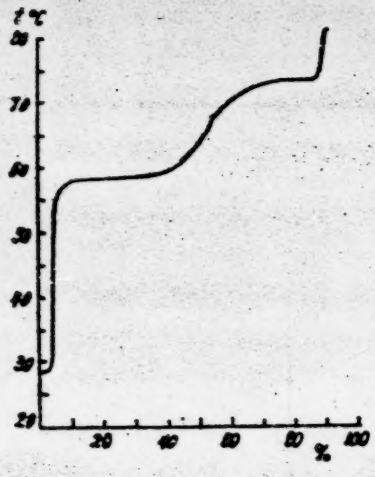

Fig. 4. Fractionation curve for the product of the hydrocondensation of carbon monoxide with 2,3-dimethyl-2-butene.

Experiments with 2,3-Dimethyl-2-butene. 2,3-Dimethyl-2-butene (63.5 ml, i.e., 0.53 mole) was passed for eight hours from the buret to the reaction tube at a space velocity of 0.37 liter/liter·hr. Simultaneously a mixture of H_2 and CO (20.9 liters and 2.4 liters respectively) was passed into the catalysis tube at a space velocity of 116 liters/liter·hr. The gas-vapor phase had the following composition by volume: 34.0% 2,3-dimethyl-2-butene, 59.2% H_2, 6.8% CO. The products were 63.7 ml of liquid condensate and gas containing 0.1 liter CO, 0.2 liter CO_2, 5.0 liters H_2, and 3.2 liters saturated hydrocarbons; the gas contraction was 65%. The liquid catalyzate was dried over anhydrous copper sulfate, and 52 ml of it was fractionated at 745 mm through the same column. The fractionation curve (Fig. 4) shows that 92% by volume of the catalyzate distilled within the range 28-81°. The residue boiling above 81° comprised 7% of the total; it was distilled from a Favorsky flask over the range 84-137°, and the further residue that then remained amounted to 1%.

The fractions taken and their properties are given in Table 3. Fractions obtained in amounts of less than 0.3% are not given in Table 3.

It will be seen from Fig. 4 and Table 3 that the catalyzate consisted mainly of unchanged 2,3-dimethyl-2-butene and its hydrogenation product, 2,3-dimethylbutane. Fractions III and IV and most of Fraction II were 2,3-dimethylbutane (b.p. 58°, d_4^{20} 0.6616, n_D^{20} 1.3750 [6]). Fraction VI and much of Fraction V consisted of unchanged 2,3-dimethyl-2-butene. Fraction I and part of Fraction II contained C_5 hydrocarbons. Fraction VII may be considered to have resulted from hydrocondensation. This fraction, which comprised 11.5% by volume, was obtained from 2,3-dimethyl-2-butene, for calculation shows that not more than 1 ml of catalyzate could be obtained by synthesis from CO and H_2. These results show that 2,3-dimethyl-2-butene enters into hydrocondensation with carbon monoxide to the extent of only 10%; hydrogenation with formation of 2,3-dimethylbutane occurs to the extent of about 50%.

SUMMARY

1. The behavior of 2-methyl-2-butene and 2,3-dimethyl-2-butene in the reaction of hydrocondensation with carbon monoxide has been investigated.

2. It has been found that 2-methyl-2-butene enters into the hydrocondensation reaction to an extent of only 5-6%, and undergoes hydrogenation to 2-methylbutane to the extent of 30-35%.

3. Under the conditions of the hydrocondensation reaction, 2,3-dimethyl-2-butene is hydrogenated to 2,3-dimethylbutane to the extent of about 50%. About 10% of it undergoes the hydrocondensation reaction.

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EFFECT OF COMPRESSION ON THE PROPERTIES OF DEHYDROGENATION AND DEHYDRATION CATALYSTS

L. F. Vereshchagin, L. Kh. Freidlin, I. U. Numanov and S. G. Kulikov

Only a few data are available in the literature concerning the behavior of catalysts that have been subjected to compression under high pressures [1], and the few catalysts that have been examined were of a mixed type. In this, as in the previous investigations [2, 3], a study has been made of the effect of compression on simple, one-component catalysts, namely, zinc, titanium, and thorium oxides, and normal calcium phosphate in the dehydrogenation and dehydration reactions that are characteristic for these catalysts.

EXPERIMENTAL

Experimental Conditions

The catalyst was placed in a tube of pure aluminum, length 50 mm, diameter 10 mm. The tube was closed, placed in the channel of the multiplier, and subjected to a pressure of 20,000 atm. The compression procedure has been described in detail in a previous communication [2].

The compressed tube was cut along its length, and the catalyst was taken out. The reaction was performed by the continuous-flow method with 10 ml of catalyst. The experimental conditions and results are given in the tables.

Dehydrogenation of Isobutyl Alcohol over Zinc Oxide

The data in the literature on the catalytic selectivity of zinc oxide are contradictory. Zinc oxide is generally regarded as a dehydrogenation catalyst, but Adkins [4] has succeeded in preparing samples of zinc oxide having dehydration properties. He explained this great change in the selectivity of this oxide catalyst by peculiarities in the conditions of its preparation and treatment. Agronomov [5] has studied this subject and has concluded that the varying activity of zinc oxide samples in the dehydrogenation of isobutyl alcohol are due not to differences in the parameters of the crystal lattice, but to variations in specific surface.

Kutseva [6] found that zinc oxide, free from any promoter, selectively catalyzed the dehydrogenation of isobutyl alcohol. Variation in the method of preparation of the zinc oxide and its treatment with ultraviolet radiation or X-rays had no effect on its selectivity; only the addition of foreign substances affected its specificity. According to these results, it was to be expected that compression also would not affect the selectivity of the action of zinc oxide.

TABLE 1

Dehydrogenation of Isobutyl Alcohol over Noncompressed and Compressed Zinc Oxide

Catalyst	Temperature of experiment (°C)	Volume of gas evolved per 1 ml of alcohol (ml)	Composition of gas* (%)			Degree of conversion of alcohol (%)
			CO_2	CO	H_2	
Noncompressed 10 ml, 5.6 g	340	50.4	1.2	0.2	98.6	20.6
	360	114.1	1.2	0.3	98.5	47.2
	380	196.3	1.2	0.4	98.4	79.5
Compressed 10 ml, 18.5 g	340	83.6	1.2	0.2	98.6	33.8
	360	166.1	1.2	0.2	98.6	67.7
	380	240.2	1.4	0.9	97.7	97.1

*No saturated or unsaturated hydrocarbons were detected in the gas.

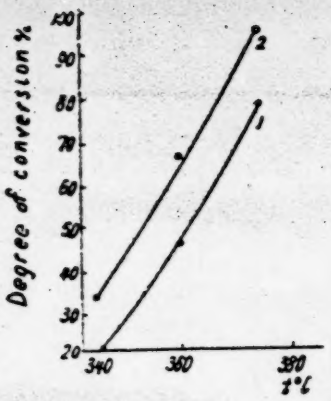

Fig. 1. Dehydrogenation of isobutyl alcohol over ZnO: 1) noncompressed; 2) compressed.

The zinc oxide was prepared by precipitation of a molar solution of zinc nitrate with a normal solution of sodium carbonate. The precipitate was washed, molded, and heated for 10-12 hours at 350°. The specific surface of zinc oxide prepared in this manner should be about 50 sq.m/g. In all experiments the space velocity was 0.28 liter/liter·hr.

It will be seen from Table 1 that both compressed and noncompressed zinc oxide selectively catalyze the decomposition of isobutyl alcohol in the direction of dehydrogenation. At 340° the degree of conversion of isobutyl alcohol over compressed catalyst is approximately 70% higher than over noncompressed catalyst, and the corresponding figures for 360° and 380° are 45% and 24% respectively.

Both of the samples of zinc oxide were submitted to X-ray analysis (chromium K series λ = 2.285 A). The following results were obtained:

Sample before compression	a = 3.15 A and c = 5.08 A
Sample after compression	a = 3.19 A and c = 5.11 A
Data from tables	a = 3.24 A and c = 5.18 A

After compression, therefore, the parameters of the zinc oxide lattice had changed only slightly.

Kinetics of the Decomposition of Ethyl Alcohol over Titanium Dioxide

As Rubinshtein and Kulikov [7] have shown, titanium dioxide in the form of anatase preferentially catalyzes dehydration, whereas the rutile form favors dehydrogenation; also, the pure forms taken separately are less active than a mixture of the two. Under the temperature conditions necessary for the decomposition of alcohol, both modifications of titanium oxide are generally present.

On account of the tendency of titanium dioxide to undergo polymorphic changes, it was of interest to find out whether any such change could take place during compression, and so affect its catalytic activity and specificity in the decomposition of ethyl alcohol. The titanium oxide was prepared from titanium tetrachloride by precipitation with dilute aqueous ammonia.

The results obtained are given in Table 2 and Fig. 2-5.

TABLE 2

Decomposition of Ethyl Alcohol over Compressed and Noncompressed Titanium Dioxide.

Catalyst	Temperature of experiment (°C)	Volume of gas evolved per 1 ml of alcohol (ml)			Degree of conversion (%)			Heat of dehydrogenation (cal/mole)
		H_2	C_2H_4	C_2H_6	Dehydrogenation	Dehydration	Total	
Noncompressed: Vol. 10 ml, Wt. 8.8 g	360	14.3	82.5	60.6	19.5	37.0	56.5	7200
	380	18.6	105.7	68.8	22.7	45.5	68.2	
	400	28.0	110.2	76.8	27.3	48.7	76.0	
Compressed: Vol. 10 ml, Wt. 17.5 g	360	13.0	115.1	46.0	15.0	42.3	57.3	7200
	380	17.4	118.3	48.2	16.8	43.0	59.8	
	400	21.8	106.9	58.6	21.0	43.0	64.0	

It will be seen from Table 2 that, apart from the products of the two main reactions (ethylene and hydrogen) ethane is formed also. Hence, in the calculation of the degree of conversion of alcohol in the two directions, the volume of ethane formed is recalculated as ethylene and hydrogen, and the values obtained are added to the analytically found volumes of ethylene and hydrogen.

It will be seen from Table 2 and Fig. 2 that the total degree of conversion of ethyl alcohol at 360° is the same over compressed catalyst as over noncompressed catalyst. With rise in temperature the degree of conversion in presence of noncompressed catalyst rises from 56.5% at 360° to 76% at 400°. In presence of compressed catalyst, however,

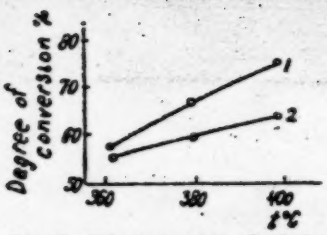

Fig. 2. Decomposition of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

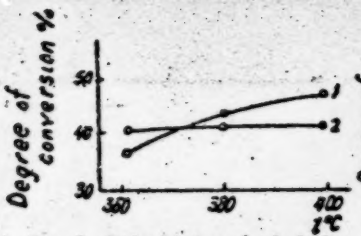

Fig. 3. Dehydration of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

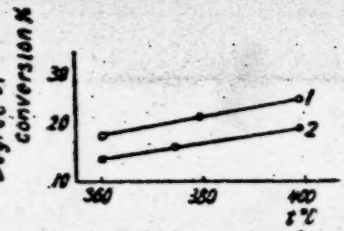

Fig. 4. Dehydrogenation of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

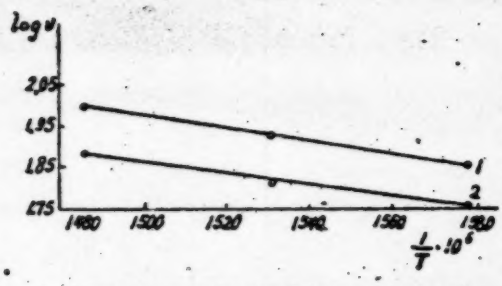

Fig. 5. Kinetic curves for the dehydrogenation of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

there is a smaller increase in the degree of conversion under these conditions: from 57.3% at 360° to 64% at 400°.

Let us examine the way in which the rates of the three different reactions vary. Over noncompressed catalyst the rate of the dehydration of alcohol rises sharply with rise in temperature, whereas over compressed catalyst it remains constant. Also, the reaction rate over the compressed sample is appreciably higher at 360°, somewhat lower at 380°, and considerably lower at 400° than the rate of the noncompressed catalyst (Fig. 3). On the other hand, dehydrogenation and hydrogenation reactions (Fig. 4) proceed at an appreciably higher rate over the noncompressed sample than over the compressed sample.

The results show that compression of the catalyst has less effect on its activity for the dehydration of alcohol than on its activity for the dehydrogenation of alcohol or hydrogenation of ethylene. The activation energy for the dehydrogenation reaction is the same for both titanium dioxide samples, and has a value of 7200 cal/mole (Fig. 5). It would appear that the reduction in rate of dehydrogenation over a compressed sample (in comparison with the rate of dehydration over the sample) is associated not with change in the nature of the active centers, but with increase in the difficulty with which the products of this reaction (mainly acetaldehyde) undergo desorption from the surface of the catalyst after it has been compressed so that the volume of the conveying pores has probably been reduced.

Kinetics of the Decomposition of Ethyl Alcohol over Thorium Dioxide

It is known that thorium dioxide is able to catalyze the decomposition of alcohols in two directions simultaneously: dehydrogenation and dehydration. The method by which it is prepared is of considerable importance. In Tolstopyatova's experiments [8] thorium dioxide prepared by precipitation of thorium nitrate with ammonia was found to catalyze the decomposition of ethyl alcohol at 300° so that mainly (85-90%) dehydrogenation occurred. When the temperature was raised to 420°, the degree of dehydrogenation fell to 40-50%, and the degree of dehydration rose from 10-12% to 40%.

We have now studied the comparative activity of compressed and noncompressed thorium dioxide prepared by precipitation of thorium nitrate with ammonia. The catalyst was washed, dried at 110-120°, and then dehydrated for 9-10 hours at 340-350°. Alcohol was passed at a space velocity of 0.75 liter/liter · hr. The results obtained are given in Table 3 and Fig. 6-9.

It will be seen from Table 3 that both compressed and non-compressed thorium dioxide samples catalyze both decomposition processes, and also the side process of carbon monoxide and carbon dioxide formation. The amount of carbon oxides in the gaseous reaction products varied from 19 to 22% for the noncompressed catalyst and from 15 to 17% for the compressed catalyst. Since this side process of carbon oxide formation occurs at almost identical rates on the two catalysts at various temperatures, the kinetics of the two main processes of alcohol decomposition may be examined independently of the rate of the side reaction. The activity of compressed thorium dioxide (per unit

TABLE 3

Decomposition of Ethyl Alcohol in Presence of Noncompressed and Compressed Thorium Dioxide

Catalyst	Temperature of expt. (°C)	Vol. of gas evolved per 1 ml of alcohol (ml)	Composition of gas (%)				Degree of conversion of alcohol		Dehydrogenation/dehydration ratio	Total conversion of alcohol (%)	Q (cal/mole)	
			CO	CO_2	C_2H_4	H_2	Dehydration (%)	Dehydrogenation (%)			Dehydrogenation	Dehydration
Noncompressed: Vol. 10 ml, Wt. 8.6 g	300	31.3	7.1	16.9	17.6	58.3	1.4	4.7	3.3	6.1	–	–
	330	88.0	10.0	10.0	20.0	60.0	4.5	13.3	3.0	17.8	–	–
	350	177.6	10.0	9.8	21.2	59.0	9.7	27.0	2.8	36.7	27 500	27 500
	370	360.0	10.0	9.0	23.0	58.0	21.3	53.5	2.5	74.8	–	–
Compressed: Vol. 10 ml, Wt. 18.0 g	300	49.1	9.0	6.3	17.2	67.5	2.7	8.5	3.1	10.7	–	–
	330	160.0	10.0	6.0	21.5	62.5	8.8	25.6	2.9	34.4	30 500	30 500
	350	312.0	10.0	6.4	23.4	60.2	18.7	48.2	2.6	66.9	–	–

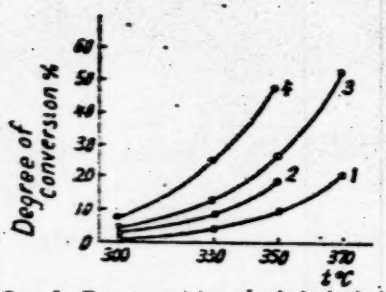

Fig. 6. Decomposition of ethyl alcohol over ThO_2: 1) dehydration over noncompressed; 2) dehydration over compressed; 3) dehydrogenation over noncompressed; 4) dehydrogenation over compressed.

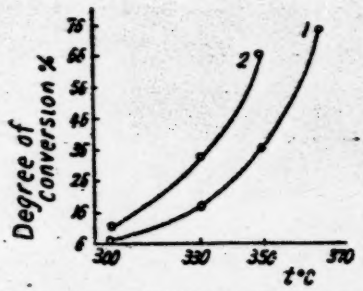

Fig. 7. Decomposition of ethyl alcohol over ThO_2: 1) noncompressed, 2) compressed.

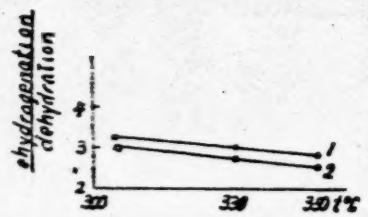

Fig. 8. Dehydrogenation/dehydration ratio for ethyl alcohol over ThO_2: 1) noncompressed; 2) compressed.

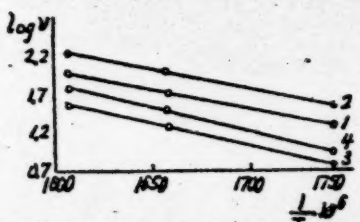

Fig. 9. Kinetic curves for the decomposition of ethyl alcohol over ThO_2: 1) dehydrogenation over noncompressed; 2) dehydrogenation over compressed; 3) dehydration over noncompressed; 4) dehydration over compressed.

TABLE 4

Kinetics of the Dehydration of Formic Acid over Noncompressed and Compressed Normal Calcium Phosphate

Catalyst	Temperature of experiment (°C)	Volume of gas evolved per 1 ml of acid (ml)	Degree of dehydration of acid (%)	Q (cal/ mole)
Noncompressed: Vol. 10 ml, Wt. 5.8 g	180	90.8	15.3	14 300
	188	113.2	19.6	
	194	146.0	24.9	
	200	174.6	30.2	
	204	200.0	34.6	
	214	260.0	45.0	
Compressed: Vol. 10 ml, Wt. 12.8 g	204	122.3	21.1	14 300
	194	91.1	15.7	
	216	179.0	30.8	
	188	69.4	12.2	
	214	162.8	28.1	

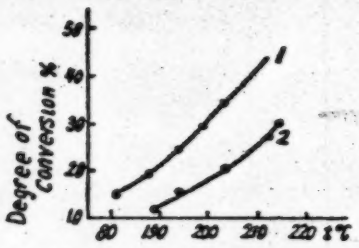

Fig. 10. Decomposition of HCOOH over $Ca_3(PO_4)_2$: 1) noncompressed; 2) compressed.

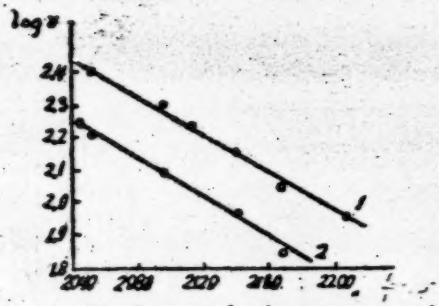

Fig. 11. Kinetic curves for the dehydration of HCOOH over $Ca_3(PO_4)_2$: 1) noncompressed; 2) compressed.

volume) is greater than that of the noncompressed catalyst in both reactions, dehydrogenation and dehydration (Fig. 6). The overall rate of decomposition of alcohol is also greater for the compressed catalyst than for the noncompressed catalyst (Fig. 7).

The ratio of the degrees of dehydrogenation and dehydration of alcohol over the range 300-350° remains almost constant for both samples of thorium dioxide (Fig. 8). This indicates that compression does not affect the selectivity in the action of the catalyst. In Fig. 9 the conformity with the Arrhenius equation is shown for the two reactions over the range 300-350°. The activation energies of the two reactions are the same on compressed and noncompressed catalyst: Q_{H_2} = 27,500 cal/mole and Q_{-H_2} = 30,000 cal/mole.

Kinetics of the Dehydration of Formic Acid over Normal Calcium Phosphate

As the work of Freidlin and Levit has shown, calcium phosphate is an extremely active catalyst of exceptionally high selectivity for the reaction of the dehydration of formic acid [9]. Already at 276° formic acid (concentration 82%) undergoes complete conversion (the carbon monoxide content of the gas obtained is 100%). The apparent activation energy of the reaction is 15,200 cal/mole.

In this work we again used a catalyst prepared from calcium chloride and ammonium phosphate; and we again used 82% formic acid. In all experiments the rate of passage of acid was 1.5 liters/liter·hr.

As will be seen from Table 4, the catalyst fully retained its high specificity when compressed: the carbon monoxide content of the gas was 100%, and there were no side processes.

The results show that after compression the activity of the catalyst is reduced by a factor of 1.5-2, when expressed in terms of unit volume, and by a factor of 3-4, when expressed in terms of unit weight (Fig. 10). The

apparent activation energy for the reaction is the same as that for the noncompressed catalyst, and has the value 14,300 cal/mole (Fig. 11). Both of the catalyst samples were investigated by X-rays (chromium K series, λ = = 2.285 A). No change in crystal structure could be detected.

SUMMARY

1. A study has been made of the effect of compression at 20,000 atm on the properties of zinc oxide, titanium dioxide, thorium dioxide, and normal calcium phosphate in dehydrogenation and dehydration reactions characteristic for these catalysts.

2. It has been shown that as a result of compression the apparent specific volume of these catalysts is reduced by the factors indicated:

Zinc oxide	3.3
Titanium dioxide	2.0
Thorium dioxide	1.5
Calcium phosphate	2.2

3. The selectivities in the action of zinc oxide in the dehydrogenation of isobutyl alcohol and in the action of calcium phosphate in the dehydration of formic acid were fully retained after compression. In the case of thorium dioxide also, compression had no effect on the relative rates of the two courses of the decomposition of ethyl alcohol. On the other hand, in presence of compressed titanium dioxide the ratio of the degree of dehydrogenation of alcohol to its degree of dehydration is lower than in presence of the noncompressed sample. It is probable that the change in the specificity of titanium dioxide due to compression is associated with change in its porosity characteristics and with the difficulty with which the dehydrogenation product (acetaldehyde) is desorbed from the catalyst.

4. In all cases the activation energy of the reaction is the same, whether the catalyst is compressed or not.

5. The activities of the investigated catalysts were altered in various ways by compression. The activity per unit weight was reduced for all catalysts apart from thorium dioxide, but the activity per unit volume rose for all catalysts except calcium phosphate, the activity of which was halved.

6. None of the investigated catalysts underwent any change in crystal structure when compressed.

I am grateful to A. M. Rubinshtein for the X-ray analysis of the catalysts.

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STABILIZATION OF α-HALO ETHERS

M. F. Shostakovsky and A. V. Bogdanova

The high reactivity of the α-halo ethers of general formula $CH_2-CH\,Hal-OR$ (R = Alk or Ar), which have been previously synthesized and investigated by us [1, 2, 3], is being made use of to an increasing extent in the synthesis and investigation of various vinyl ether derivatives. A serious obstacle to the wider application of these compounds is their extreme instability in comparison with alkyl halomethyl ethers of formula $CH_2Hal-OAlk$ [4].

Experiments with many of these ethers have shown that decomposition of the initially pure ether sets in already after three hours in a sealed tube; after three weeks decomposition is complete. On this account we have carried out experiments on the stabilization of α-halo ethers, and, as a result, we have discovered conditions under which they may be kept for a long time. By use of this method of preservation it is no longer necessary to use all of a synthesized sample of α-halo ether immediately; it may be used a little at a time in a series of experiments.

α-Halo ethers can be readily preserved in the pure state at below 0°, but this method is inconvenient in practice, so that the most satisfactory method of preservation would appear to be one in which solvent stabilizers are used. The properties and reactions of α-halo ethers show [2, 3] that the bromo compounds are the least stable, and we therefore carried out most of our experiments on the selection of a solvent (stabilizer) with these ethers, on the assumption that a stabilizer suitable for α-bromo ethers would undoubtedly be suitable also for α-chloro ethers.

It has been noted previously [5] that the keeping of pure 1-bromoethyl butyl ether in diffused light at room temperature for three weeks is accompanied by its complete decomposition into butyl bromide and water. This decomposition of 1-bromoethyl butyl ether at room temperature in diffused light begins already after three hours. Our experiments have shown that an addition of only 15-20% of diethyl ether to 1-bromoethyl butyl ether enables it to be preserved at room temperature for two months or more.

1-Chloroethyl ethyl ether with an addition of 25% of diethyl ether, was preserved in a sealed tube at room temperature for four years. It is interesting that, when the contents of the tube were distilled, apart from 1-chloroethyl ethyl ether, high-boiling products were isolated that were not only α-substituted, but also β-substituted. It may be supposed that acetal formation occurred, accompanied by the replacement of β-hydrogen atoms by chlorine atoms in a manner similar to the successive entry of chlorine into the α- and β-positions in the diethyl ether molecule [7, 8]. Satisfactory results were obtained also by the use of benzene and dioxane as solvent stabilizers: the keeping life of 1-bromoethyl butyl ether at room temperature in presence of 20% of these substances was more than one month.

α-Halo ethers are particularly sensitive to reaction at elevated temperatures [5, 6]. It has been shown [5] that heating of pure 1-bromoethyl butyl ether at 80-100° is accompanied by its complete decomposition, when it gives butyl bromide in 97.1% yield. Since most of the syntheses with α-halo ethers are carried out at elevated temperatures, it was of particular interest to find the conditions for the stabilization of α-halo ethers at such temperatures. By the use of the proposed solvent stabilizers it was found possible to preserve α-bromo ethers for more than one and a half months. The experiments showed that for the stabilization of α-halo ethers at elevated temperatures greater amounts of solvent stabilizer were required, as compared with that required at room temperature.

EXPERIMENTAL

The α-halo ethers used had the constants given in Table 1.

The following solvents were examined as stabilizers: dioxane, petroleum ether, benzene, diethyl ether. These substances were used in the absolute form. The change in the color of the solution of α-halo ether served as an outward sign of decomposition. By way of example we now cite a few experiments on the stabilization of α-halo ethers.

TABLE 1
Constants of α-Halo Ethers

Ether	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
1-Chloroethyl ethyl ether	34-35 (64)	1.4040	0.9493
1-Bromoethyl ethyl ether	40-41 (42)	1.4465	1.2770
1-Bromoethyl butyl ether	57-58 (10)	1.4485	1.2086

1. Stabilization of 1-Bromoethyl Butyl Ether at Room Temperature. 1-Bromoethyl butyl ether (3 g) and 0.5 g (17%) of the solvent stabilizer were sealed in a 10-ml tube. The tube was kept in diffused light at room temperature. The change in the color of the solution with time will be seen from Table 2.

TABLE 2
Change in the Color of Solutions of 1-Bromoethyl Butyl Ether kept at Room Temperature

Tube No.	Solvent stabilizer	Time of keeping	
		1 month	2 months
1	Benzene	Pink	Brown
2	Dioxane	Faintly pink	Brown
3	Diethyl ether	Colorless	Colorless

The contents of the tubes were vacuum-distilled, and yielded: Tube No. 3, 2.8 g of 1-bromoethyl butyl ether, b.p. 59-60° (12 mm); n_D^{20} 1.4480; d_4^{20} 1.2082. Each of Tube No. 1 and No. 2, 2.5 g of 1-bromoethyl butyl ether having the same constants as the starting material.

2. Stabilization of 1-Bromoethyl Butyl Ether at 60°. In each 10-ml tube, 3 g of 1-bromoethyl butyl ether and 3 g of solvent stabilizer were sealed, and the tubes were kept in diffused light at room temperature for two weeks, and were then placed in a thermostat and left there at 60° for five weeks. After the two weeks in diffused light at room temperature, all of the solutions remained colorless, and changes in color occurred only during storage at 60°, as shown in Table 3.

TABLE 3
Change in the Color of Solutions of 1-Bromoethyl Butyl Ether kept at 60°.

Tube No.	Solvent stabilizer	Time of keeping		
		1 day	4 weeks	5 weeks
1	Benzene	Slightly colored	Dark-colored	Black
2	Dioxane	Slightly colored	Dark-colored	Black
3	Diethyl ether	Colorless	Colorless	Dark-colored

The contents of the tubes were vacuum-fractionated, and yielded: Tube No. 3, 2.7 g of 1-bromoethyl butyl ether, b.p. 70-71.5° (22 mm), n_D^{20} 1.4478; d_4^{20} 1.2083. Tubes No. 1 and 2, 2.2 g and 2.5 g respectively of 1-bromoethyl butyl ether having the same constants as the starting material.

3. Stabilization of 1-Bromoethyl Ethyl Ether at Room Temperature. A mixture of 3 g of 1-bromoethyl ethyl ether and 0.5 g (17%) of solvent stabilizer was sealed in each tube, and the tubes were kept at room temperature in diffused light. The changes of color with time are indicated in Table 4.

TABLE 4
Change in Color of Solutions of 1-Bromoethyl Ethyl Ether kept at Room Temperature

Tube No.	Solvent stabilizer	Time of keeping	
		1 week	4 weeks
1	Dioxane	Colorless	Dark-colored
2	Petroleum ether	Pink	Dark-colored
3	Benzene	Yellow	Dark-colored
4	Diethyl ether	Colorless	Slightly pink

The contents of the tubes were vacuum-fractionated, and yielded:: Each of Tubes 1, 2, and 3, 2.5 g of 1-bromoethyl ethyl ether. Tube 4, 2.8 g of the ether. The constants of all of the samples of 1-bromoethyl ethyl ether recovered were identical with those of the starting material.

4. Stabilization of 1-Chloroethyl Ethyl Ether at Room Temperature. A mixture of 20 g of 1-chloroethyl ethyl ether and 5 ml (25%) of diethyl ether was sealed in a tube and kept at room temperature in diffused light. The tube was kept in the laboratory from November 29, 1948, to August 29, 1952. The contents became darker in color, but no precipitate formed. Vacuum fractionation yielded 7.5 g (38%) of 1-chloroethyl ethyl ether, b.p. 30-31.5° (61 mm); n_D^{25} 1.4040; d_4^{25} 0.9492. The higher-boiling fractions yielded 6.2 g of a product having the following constants: b.p. 71-72° (17 mm); n_D^{25} 1.4320; d_D^{25} 1.0432; Found MR 37.95; Calculated for acetaldehyde chloroethyl ethyl acetal MR 38.05

Found M: 161.0, 163.8

$C_6H_{13}O_2Cl$ Calculated M: 152.62

Total Cl content (combustion)	29.65%
Cl^- content (titration)	11.9 %
H^+ content (titration with 0.1 N NaOH)	0.355%
H^+ content (Calculated from Cl^- content)	0.338%

This product was treated with dilute caustic soda, washed with water until neutral, and extracted with benzene. The extract was dried over $CaCl_2$, and the benzene was distilled off. Vacuum distillation of the residue yielded a fraction of b.p. 66-67° at 22 mm and n_D^{20} 1.4273. This substance did not have a sharp odor and gave no precipitate with silver nitrate, but it gave a positive Beilstein test for halogen. The chlorine content of this fraction (by combustion) was 17.68%.

Owing to the small amount of the substance isolated, it was unfortunately impossible to investigate it in greater detail, but the results obtained permit us to suppose that it consisted of a mixture of the 1- and 2-chloroethyl ethyl acetals of acetaldehyde.

SUMMARY

1. The conditions have been determined for the stabilization of α-halo ethers, so enabling them to be kept both at room and at elevated temperature.

2. An addition of 15-20% of diethyl ether to an α-halo ether stabilizes it at room temperature for a period of from two months to four years. Addition of 50% of diethyl ether enables α-halo ethers to be kept for two months at elevated temperatures.

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** See Consultants Bureau Translation, page 1367.

*** See Consultants Bureau Translation, page 1379.

**** See Consultants Bureau Translation, page 429.

***** See Consultants Bureau Translation, page 435.

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REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 1. REACTIONS OF ALKYL VINYL ETHERS WITH GLYCEROL

M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya

This communication is the first of a series on our investigations on the reactions between various vinyl compounds of general formula $CH_2 = CH - R$ (R may be OAlk, OR, OCOR, Hal, SR, NR_2, etc.) and various multifunctional compounds containing hydroxyl, carboxyl, and other functional groups.

The reactions between vinyl ethers and substances containing various functional groups provide a valuable method for the synthesis of a number of new compounds.

The course of the reaction between vinyl ethers and alcohols, phenols, acids, or other analogous compounds may be represented as follows:

$$CH_2 = CH - OR + HOR' \longrightarrow CH_3 - CH(OR)(OR_1),$$

(R and R_1 may be alkyl, aryl, acyl, etc.).

These reactions are of interest not only from the point of view of synthesis, but also for the study of the properties and reactions of the original vinyl ethers and compounds containing a mobile hydrogen. Some considerable investigation has been made into the course of the reactions of alkyl vinyl ethers with monohydric alcohols having primary or secondary hydroxyl groups.

An investigation of the conditions under which polyhydric alcohols add to alkyl vinyl ethers was of particular interest. It is known from previous investigations by Shostakovsky and coworkers [1, 2, 3] that the addition products formed by monohydric alcohols with alkyl vinyl ethers are acetals of the following structures:

$$CH_3 - CH(OR)(OR) \quad \text{and} \quad CH_3 - CH(OR)(OR_1)$$

The structure (1) and disproportionation (2) of the acetals can be illustrated by the following schemes:

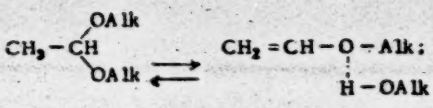
$$CH_3 - CH(OR)(OR) \rightleftharpoons CH_2 = CH - O - R \quad (H - OR) \qquad (1)$$

$$2CH_3 - CH(OR)(OR_1) \longrightarrow CH_3 - CH(OR)(OR) + CH_3 - CH(OR_1)(OR_1) \qquad (2)$$

The tautomerism of acetals results from the mobilities of hydrogen atoms, both the hydrogen of the methyl of the aldehyde residue and the hydrogen of the hydroxyl of the alcohol. An interesting special case is presented by mixed acetals containing both an alkoxyl and an aryloxyl radical:

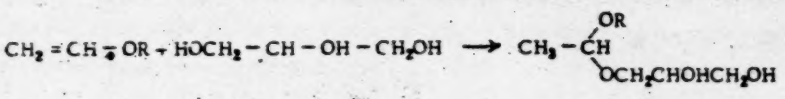
$$CH_3 - CH(OAlk)(OAr) \longrightarrow CH_2 = CH - O - Alk \quad (H - O - Ar) \leftarrow$$

Here equilibrium is greatly displaced to the right, owing to the fact that phenols contain hydrogen of greater mobility. Dialkyl acetals (in which the alkyls may be the same or different) also exist in two tautomeric forms:

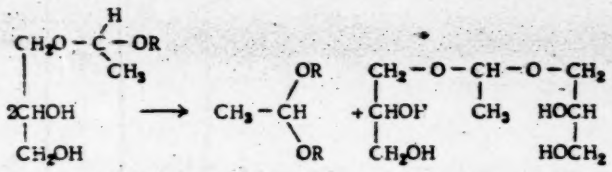


but in this case the point of equilibrium is different, being in the direction of the classical acetal structure.

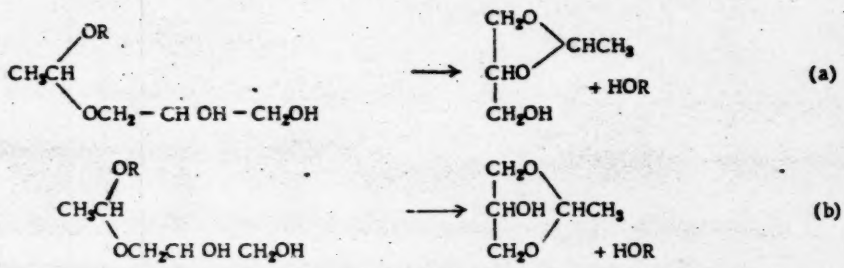
Particular interest is presented by the synthesis and reactions of acetals in which one alcohol residue is derived from a polyhydric alcohol, such as glycerol. When ethyl vinyl or ethyl butyl ether reacts with glycerol (equimolecular ratio of reactants), the first reaction should be as follows:



(R is C_2H_5 or C_4H_9). The resulting acetal may behave in two different ways, i.e., either undergo disproportionation according to the scheme:

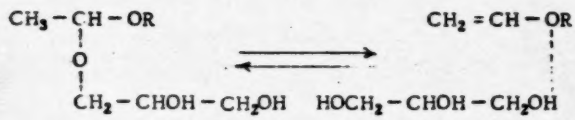


or undergo cyclization according to schemes (a) or (b):



It was found that in practice the rate of cyclization is greater than that of disproportionation. Our main products in the reaction of ethyl vinyl ether with glycerol were the 1,2 and 1,3 cyclic acetals of glycerol (which we shall refer to as 1,2- and 1,3-O-ethylideneglycerol respectively) and ethanol, only very small amounts of acetaldehyde diethyl acetal being obtained. In the reaction of butyl vinyl ether with glycerol, 1,2-O-ethylideneglycerol and butyl alcohol were isolated. The formation of only 1,2-O-ethylideneglycerol is evidently to be explained by the lower mobility of the alcohol radical of butyl vinyl ether.

The mechanism of the formation of mixed acetals of ethyl alcohol and glycerol can be represented as follows:

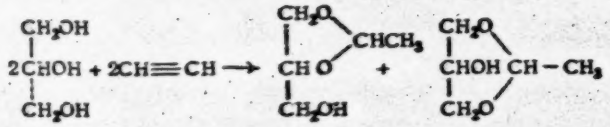


This is in its essence tautomerism. It is to be expected that the hydrogen bond will be formed at the expense of the more mobile hydrogen of one of the glycerol hydroxyl groups.

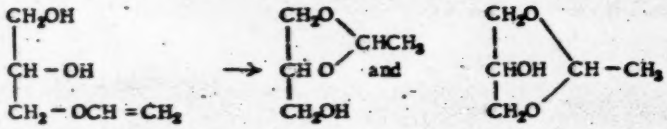
In the present investigation we have obtained twice as much 1,2-O-ethylideneglycerol as 1,3-O-ethylideneglycerol. This difference may result from the fact that, owing to its spatial proximity, the hydrogen of the 2-hydroxyl

group is the first to react, and is followed by the hydrogen of the 1-hydroxyl. These considerations relating to the displacement of alkoxyl groups from mixed acetals by free hydroxyls of glycerol are fully in accord with previous investigations of one of us and coworkers [4].

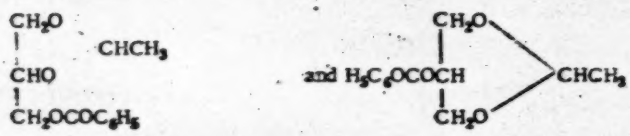
Nieuwland and coworkers [5, 6] have obtained 1,2- and 1,3-O-ethylideneglycerols by the reaction of glycerol with acetylene in presence of HgO and BF_3:



Shostakovsky and Gracheva [7] have prepared the same acetals by the cyclization of glycerol monovinyl ether under the action of heat and traces of mineral acid:



In the present work we have shown that unsymmetrical mixed acetals containing alkoxyl groups and free hydroxyls derived from glycerol undergo cyclization as a result of interaction between the alkoxyl group and one of the hydroxyls of the glycerol, an alcohol being eliminated and the corresponding cyclic acetal formed. The separation of the resulting isomeric acetals was effected by the aid of benzoylation, the compounds



being isolated; their hydrolysis products corresponded in constants to 1,2- and 1,3-O-ethylideneglycerols.

EXPERIMENTAL

Starting Materials: The alkyl vinyl ethers were prepared by Favorsky and Shostakovsky's method; ethyl vinyl ether, b.p. 35-36°; n_D^{20} 1.3782; d_4^{20} 1.7533; butyl vinyl ether, b.p. 92-93°; n_D^{20} 1.4030; d_4^{20} 0.7795; glycerol had b.p. 164-172° (8-14 mm); n_D^{20} 1.4728; d_4^{20} 1.2582.

Reaction of Ethyl Vinyl Ether with Glycerol

A mixture of 14.4 g (0.2 mole) of ethyl vinyl ether and 18.4 g (0.2 mole) of glycerol was placed in a three-necked flask fitted with mercury-sealed stirrer, condenser, and thermometer. It was then stirred for 30 minutes, when one drop (0.014 g of HCl) of catalyst was added. In the course of 30 minutes the temperature gradually rose from 23° to 35°, and then rose sharply to 76.5°. The reaction yielded 31.9 g of product.

The reaction mixture was neutralized with potassium carbonate and distilled from a Favorsky flask. From 29.03 g the following fractions were obtained

Fraction I	b.p. 76-77°; 7.5 g
Fraction II	b.p. 76-93° (11-12 mm); 17.8 g
Residue	3.4 g

a) Investigation of Fraction I. The fraction smelled of acetal, but reacted vigorously with sodium. Agulhon's qualitative test [8] on a trial sample gave a color almost the same in intensity as that obtained in a parallel test on pure ethyl alcohol. The constants of the fraction (n_D^{20} 1.3660 and d_4^{20} 1.7980) and qualitative tests all indicated that Fraction I consisted essentially of ethyl alcohol containing some acetaldehyde diethyl acetal, the separation of which did not appear to be possible. For ethyl alcohol the literature gives n_D^{20} 1.361 and d_4^{20} 0.789. The yield of the fraction, regarded as ethyl alcohol, was 92.5%.

b) Investigation of Fraction II. Fraction II had the following constants: n_D^{20} 1.4448; d_4^{22} 1.1260. A second fractionation under reduced pressure did not give any clear resolution of the product. It was found to contain free hydroxyl groups.

In order to resolve Fraction II it was benzoylated. A mixture of the fraction (15 g; dried with potassium carbonate) with 36 g of pyridine (dehydrated and distilled over BaO; b.p. 114-115°) was placed in a flask which was closed with a stopper carrying a dropping funnel protected by a calcium chloride tube. Freshly distilled benzoyl chloride (15 g; b.p. 75-76° at 10-11 mm) was added slowly from the dropping funnel with shaking. Reaction was accompanied by evolution of much heat. After 30 minutes the mixture was poured into 300 ml of distilled water, and the oily product was extracted with ether. The ether extract was washed successively with 5% KOH, 3% H_2SO_4, and water (until neutral), and was then dried with calcined potassium carbonate. The ether was driven off, and the oil that remained behind was heated at 100° in a vacuum to remove traces of pyridine. To this mixture of benzoic esters 30 ml of gasoline (b.p. 50-60°) was added, and the solution was cooled to −12°. The crystals that were then precipitated were filtered off through a cooled funnel, and the liquid benzoic ester remaining after removal of gasoline was vacuum-distilled. In this way 5.9 g of crystalline benzoic ester and 11.36 g of liquid benzoic ester were obtained, the total yield of benzoic esters being 17.26 g (61%).

c) Characterization of the Benzoic Esters. After recrystallization from gasoline the crystalline benzoic ester melted at 85°. For the benzoic ester of 1,3-O-ethylideneglycerol the literature [6] gives m.p. 86°.

Found: M 224.1
$C_{12}H_{14}O_4$ Calculated: M 222*

Found %: C 64.54; 64.76; H 6.48; 6.46
$C_{12}H_{14}O_4$ Calculated %: C 64.83; H 6.31

After a second freezing treatment and redistillation, the liquid benzoic ester had the following constants: b.p. 161-162° (9-10 mm); d_4^{20} 1.1558 and n_D^{20} 1.5140. The literature [6] gives b.p. 163-164° (11-12 mm); n_D^{17} 1.5145; d_4^{17} 1.1618.

Found: M 220
$C_{12}H_{14}O_4$. Calculated: M 222

Found %: C 65.87; 64.63; H 6.41; 6.46
$C_{12}H_{14}O_4$. Calculated %: C 64.83; H 6.31

Preparation of 1,3-O-Ethylideneglycerol by Hydrolysis of its Benzoic Ester

The crystalline 1,3-O-ethylideneglycerol benzoic ester (2.2 g; m.p. 85°) was heated and stirred with 15 ml of 10% KOH until solution was complete. To the clear cooled solution 8 g of calcined potassium carbonate was added, and it was then subjected to repeated extraction with ether. The ether extract was dried with calcined potassium carbonate, and the ether was distilled off, yielding 0.41 g (35%) of product, b.p. 66-68° (11-12 mm); n_D^{20} 1.4536; $n_D^{16.5}$ 1.4538. For 1,3-O-ethylideneglycerol the literature [6] gives b.p. 52° (2 mm); n_D^{17} 1.4532.

Found %: C 50.81; 50.95; H 8.81; 8.77
$C_5H_{10}O_3$. Calculated %: C 50.84; H 8.47

Preparation of 1,2-O-Ethylideneglycerol by Hydrolysis of its Benzoic Ester

The liquid ethylideneglycerol (8.06 g), treated in a similar way, yielded 1.74 g (43%) of a product of b.p. 84-85° (11-12 mm); n_D^{20} 1.4436. For 1,2-O-ethylideneglycerol the literature [6] gives b.p. 68-70° (1 mm); n_D^{17} 1.4415; d_4^{17} 1.1248.

Found %: C 50.34; 50.14; H 8.61; 8.51
$C_5H_{10}O_3$. Calculated %: C 50.84 H 8.47

When 3 moles of ethyl vinyl ether reacted with 1 mole of glycerol, no 1,2- or 1,3-O-ethylideneglycerol was isolated. The reaction products were ethyl alcohol, acetaldehyde diethyl acetal, and bisethylideneglycerol. Study of these reaction products continues.

Reaction of Butyl Vinyl Ether with Glycerol

A mixture of 25.04 g (0.25 mole) of butyl vinyl ether and 23 g (0.25 mole) of glycerol was stirred as in the previous experiment for 30 minutes. Catalyst was added (3 drops, i.e., 0.042 g. of HCl), but no rise of temperature

* The molecular weight was determined by the Rast-Munster method.

was observed after one hour; the mixture was, therefore, heated to 50°. After 30 minutes at 50° rise in temperature was observed, 61° being attained in five minutes in absence of applied heat. The emulsion formed by the reactants was converted into a homogeneous clear solution, and when this occurred there was an immediate fall in temperature by 5° (to 56°). The reaction yielded 47.72 g of product.

The reaction product was neutralized with potassium carbonate and distilled from a Favorsky flask, when 45 g yielded the following fractions:

Fraction I, b.p. 113-114°:	16.9 g; n_D^{20} 1.4120
Fraction II, b.p. 95-103°; (23-25 mm):	23.01 g; n_D^{20} 1.4368
Fraction III, Residue	3.13 g; n_D^{20} 1.4755

a) Investigation of Fraction I. Fraction I reacted vigorously with sodium. Redistillation yielded 11.87 g (64.2%) of a product of b.p. 116-117°; n_D^{20} 1.4030; d_4^{20} 0.8232, having the characteristic odor of butyl alcohol. Agulhon's test [8] was positive for alcohol. For butyl alcohol the literature gives b.p. 117.7°; d_4^{20} 0.810; n_D^{20} 1.3993.

b) Investigation of Fraction II. Fraction II, boiling range 95-103° at 23-25 mm, n_D^{20} 1.4368, was benzolated 20 g of the fraction being added to a mixture of 48 g of pyridine and 24 g of benzoyl chloride. When treated as described above (cooling of a solution of the benzoic ester in 50 ml of gasoline), no precipitate of a crystalline product was obtained. Vacuum fractionation after removal of gasoline yielded:

Fraction I, b.p. 100-152° (12 mm):	8.18 g; n_D^{20} 1.5072
Fraction II, b.p 160-161° (12 mm):	29.98 g; n_D^{20} 1.5152
Fraction III, Residue	2.12 g; n_D^{20} 1.5268

Fraction I was redistilled and yielded a product boiling at 90 - 118° (10 - 11 mm): n_D^{20} 1.5052, which appeared to be butyl benzoate. Redistillation of Fraction II yielded a product of b.p. 159 - 160° (10 mm): n_D^{20} 1.5140; d_D^{20} 1.1617, corresponding in constants to the benzoic ester of 1,2-O-ethylideneglycerol.

Found %:	C 64.98; 65.15; H 6.39; 6.48
$C_{12}H_{14}O$. Calculated %:	C 66.6; H 6.31

Hydrolysis of this substance yielded a product of b.p. 73 - 75° (9 - 10 mm): n_D^{20} 1.4456; d_4^{20} 1.2615, corresponding to 1,2-O-ethylideneglycerol. From 7.50 g of benzoid ester taken for hydrolysis, 3.09 g (77.3%) of 1,2-O-ethylideneglycerol was obtained.

SUMMARY

A study has been made of the reactions of ethyl vinyl ether and of butyl vinyl ether with glycerol in presence of traces of hydrogen chloride, the reactants being taken in equimolecular proportions. The main reaction products were 1,2- and 1,3-O-ethylidineglycerol from ethyl vinyl ether and 1,2-O-ethylideneglycerol from butyl vinyl ether. 2. The formation of 1,2- and 1,3-O-ethylideneglycerols from ethyl vinyl ether and glycerol, and also of 1,2-O-ethylideneglycerol from butyl vinyl ether and glycerol, evidently proceeds via the formation of the corresponding mixed acetal, which then undergoes cyclization.

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* See Consultants Bureau Translation, page 643.
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BRIEF COMMUNICATIONS

SYNTHESIS OF 1-METHYL-3-PROPYLCYCLOBUTANE

B. A. Kazansky and M. Yu. Lukina

1-Methyl-3-propylcyclobutane was synthesized by the method that we have used previously for 1,3-dimethyl- and 1-ethyl-3-methyl-cyclobutane [1, 2]. It was obtained as a mixture of geometric isomers and was distilled through a 60-plate column. The two fractions, b.p. 116.1-116.3° and 118.5-118.7° (760 mm), consisted respectively of the trans and cis forms, neither being completely free from the other stereoisomer owing to the closeness of their boiling points. The results given in this note relating to their constants are therefore of a tentative character.

EXPERIMENTAL

Ethyl 3-methylcyclobutyl ketone, prepared from 3-methylcyclobutanecarboxylic acid and propionic acid by the procedure described in previous papers [1, 2], had the following constants: b.p. 164-170° (753.0 mm); n_D^{20} 1.4332; d_4^{20} 0.8757; found MR 37.44; calculated for $C_8H_{14}O$ MR 36.95; ε MR 0.49.

	Found %:	C 75.88; 75.82;	H 11.13; 11.10
$C_8H_{14}O$.	Calculated %:	C 76.11;	H 11.19

The semicarbazone of ethyl 3-methylcyclobutyl ketone was prepared by Zelinsky's method [3], and was recrystallized from aqueous methanol. After four recrystallizations it melted at 130-131.2°.

	Found %:	N 22.75; 22.75	
$C_9H_{17}N_3O$.	Calculated %:	N 23.03	

A mixture of 32 g (0.5 mole) of 85% hydrazine hydrate and 30 ml of alcohol was added slowly with stirring to a solution of 31.5 g (0.25 mole) of ethyl 3-methylcyclobutyl ketone in 35 ml of redistilled ethyl alcohol. The mixture was boiled for four hours under reflux. The alcohol and excess of hydrazine hydrate were distilled off (oil bath), the bath temperature being above 140°. The reaction mass was cooled, and a small amount of solid caustic soda was added, the water layer being then removed in a separating funnel. The hydrazone, carefully dried with caustic potash, boiled at 104-110° at 115 mm. The decomposition was carried out as usual in a Favorsky flask, attached through a condenser to a receiver and well cooled trap in the form of a coil. For the decomposition caustic potash fused in a silver dish was used; no platinum catalyst was added to the alkali in this work.

The mixture of hydrocarbon and unchanged hydrazone was again subjected to the decomposition treatment over a fresh portion of fused caustic alkali. The hydrocarbon was then washed successively with water, 50% acetic acid, 50% sulfuric acid, water, 25% caustic soda, and again water. The yield of hydrocarbon (dried with fused calcium chloride) was 16.0 g (57.1% on the ketone). In three experiments 33.7 g of hydrocarbon was obtained altogether.

The product, a mixture of cis and trans isomers, was distilled through a 60-plate column. The amount taken was 33.7 g (45 ml), and when 34.0 ml had been distilled over, 10 ml of redistilled decahydronaphthalene was added, thus enabling the higher-boiling isomer to be brought over. Distillation was at a reflux number of 50. Cuts of range 116.1-116.3° and 118.5-118.7° were taken, together with intermediate cuts. On the basis of the Auwers-Skita rule [4, 5] we assumed that the fraction of b.p. 116.1-116.3° corresponded to the trans form, and the fraction of b.p. 118.5-118.7° to the cis form of 1-methyl-3-propylcyclobutane. The properties of the stereoisomers are as follows:

trans-1-Methyl-3-propylcyclobutane: b.p. 116.1-116.3° (760 mm); n_D^{20} 1.4088; d_4^{20} 0.7370; found MR 37.60; calculated for C_8H_{16} MR 36.94; ε MR 0.66; aniline point 60.4°

	Found %:	C 85.43; 85.50;	H 14.38; 14.48
C_8H_{16}.	Calculated %:	C 85.61;	H 14.39

cis-1-Methyl-3-propylcyclobutane: b.p. 118.5-118.7° (760 mm); n_D^{20} 1.4128; d_4^{20} 0.7453; found MR 37.49; calculated for C_8H_{16} MR 36.94; ε MR 0.55; aniline point 57.2°.

	Found %:	C 85.51; 85.30;	H 14.57; 14.70
C_8H_{16}.	Calculated %:	C 85.61;	H 14.39

SUMMARY

1. 1-Methyl-3-propylcyclobutane has been prepared for the first time.

2. Some new disubstituted cyclobutanes have been prepared and characterized.

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* See Consultants Bureau Translation, page 319.

SYNTHESIS AND REACTIONS OF UNSATURATED ORGANOSILICON COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF VINYLCHLOROSILANES BY THE DIRECT METHOD

M. F. Shostakovsky and D. A. Kochkin

Unsaturated organosilicon compounds are of great theoretical interest and form a rich source for a great variety of syntheses. In this communication we describe conditions for the synthesis of vinylhalosilanes of general formula $(CH_2=CH)_nSiX_{4-n}$, in which X is a halogen (chlorine, bromine, fluorine). The example we have taken for study is the synthesis of vinylchlorosilanes. Until now the study of the synthesis of compounds of this type has been inadequate. References to methods for the preparation of unsaturated organosilicon compounds are mainly concerned with methods for their preparation with the aid of organomagnesium compounds [1-4, 6]. Attempts to prepare vinylchlorosilanes by direct synthesis from vinyl chloride and metallic silicon have not been successful [5].

Several variants are possible in the direct method for the preparation of vinylchlorosilanes, and the simplest of these appears to be the reaction of vinyl chloride with metallic silicon.

We have investigated the conditions for the direct synthesis of vinylchlorosilanes from vinyl chloride and copper-silicon alloys. In the course of these investigations we established the possibility of obtaining vinylchlorosilanes by passage of vinyl chloride over a copper-silicon alloy (20:80) at 350-400°. The scheme of reactions can be represented by the following equations:

$$4CH_2=CHCl + Si \rightarrow SiCl_4 + 8C + 6H_2. \quad (1)$$

$$3CH_2=CHCl + Si \rightarrow CH_2=CHSiCl_3 + 4C + 3H_2. \quad (2)$$

$$2CH_2=CHCl + Si \rightarrow (CH_2=CH)_2SiCl_2. \quad (3)$$

$$3CH_2=CHCl + 2Si \rightarrow CH_2=CHSiHCl_2 + CH_2=CHSiH_2Cl + 2C. \quad (4)$$

Reaction proceeds with preferential formation of trichlorovinylsilane and dichlorodivinylsilane in 35% yield. Among undesirable side reactions we may note the formation of silicon tetrachloride and a considerable amount of charcoal, resulting in great losses of vinyl chloride. Reaction proceeds with evolution of much heat; it is not very smooth.

EXPERIMENTAL

Copper-silicon alloy (20:80; 1.5 kg) in the form of 10-15-mm pieces was loaded into an iron tube, diameter 50 mm and length 1000 mm, fitted with two metal tubes for thermometer and wire stirrer. The loaded tube was placed in an electrically heated tubular muffle and heated to 350-400°. In order to dry out the alloy, dry nitrogen was passed at that temperature for 50 minutes at 1.0 liter per minute. Vinyl chloride was then passed at 0.1 liter per minute. As the synthesis proceeded, an irregular distribution of temperature in the contact mass was observed; this behavior was a result of the highly exothermic nature of the reaction, and it led to coke formation at various places in the reaction tube. In order to prevent excessive coking, it was necessary to stir. The reaction was continued for 80 hours, 480 liters of vinyl chloride being passed. The products of the synthesis (750 g) contained 70.5-71.0% of chloride ion; they contained 45-48% of trichlorovinylsilane and dichlorodivinylsilane. The crude products of the synthesis were fractionated through a two-meter column, diameter 18 mm and having a porcelain filling. The following main fractions were obtained:

Fraction I, b.p. 56-60°, yield 30.5%
Fraction II, b.p. 90-94°, yield 32.5%
Fraction III, b.p. 116-120°, yield 9.3%

Fraction II, b.p. 90-94°, was refractionated, and a fraction of b.p. 92.5-94.0° (752 mm); d_4^{20} 1.2650, was collected. It analyzed as follows:

Found %: Si 17.60; Cl 65.03
$C_2H_3SiCl_3$. Calculated %: Si 17.37; Cl 65.89

The molecular weight, determined cryoscopically in benzene, was 162.73; calculated for $C_2H_3SiCl_3$ 161.58. These results correspond to trichlorovinylsilane [7]. The yield of trichlorovinylsilane was 20.3% on the vinyl chloride taken.

Fraction III, b.p. 116-120°, was refractionated, and a fraction of b.p. 118-119° (754 mm); d_4^{20} 1.0813 was collected. It analyzed as follows:

Found %: Si 17.83; Cl 47.00
$C_4H_6SiCl_2$. Calculated %: Si 18.34; Cl 46.30

These results show that the fraction of b.p. 118-119° is essentially dichlorodivinylsilane [7], the properties and yield of which we are now studying.

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* See Consultants Bureau Translation, page a-425
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DISCUSSION

EXPERIMENTAL DETERMINATION OF ELECTRON DENSITY IN CRYSTALS*

N. V. Ageev

There can be no doubt about the enormous significance for contemporary science of the development of the theory of the structure of substances. The development of this theory is possible only by the accumulation of experimental facts on the basis of which the fundamental principles of theory can be developed. The theoretical principles so created at the same time require experimental verification and confirmation.

It will be seen from this that the development of experimental methods for the determination of the nature of the chemical bond in crystalline substances is of the highest importance. One of these methods is the determination of electron density. It would have been expected that this method would have drawn the attention of specialists and would have been developed in detail so that it might be used for the solution of problems concerning the nature of the chemical bond in crystalline substances. Actually, however, this method has been recently subjected to unmerited attacks, without being examined in a proper critical manner.

History of the Subject

We shall discuss briefly the history of the experimental determination of electron density. The method was first proposed by Bragg [1] in 1915 for the solution of questions of a purely structural nature, namely, the determination of the centers of gravity of atoms in a lattice, which correspond to maxima of electron density. The use of this method for structural purposes is now very extensive. Further development of this method resulted from Duane's work [2], in which the application of Fourier series for the calculation of electron density was greatly simplified.

The first experimental investigations on the distribution of electron density were carried out by Havinghurst [3] in 1925-1927 for sodium chloride, sodium fluoride, and lithium fluoride crystals. This method was later applied by Wollan [4] in 1930 for magnesium oxide, and by Grimm, Brill, Hermann, and Peters [5] in 1938-1944 for sodium chloride, diamond, hexamethylenetetramine, magnesium, and aluminum.

In the Soviet Union the first investigations on the determination of electron density were begun in 1940 by Breger and Zhdanov [6], who studied the nature of the chemical bond in graphite and boron nitride. In the years 1945-1952 systematic studies were made by Ageev, Guseva, and Ageeva [7-12] of the electron density in aluminum, copper, nickel, and the compounds NiAl and Mg_2Si. Finally, in 1948 Kritskaya and Rovinsky [13] obtained data for copper.

Method of Determining Electron Density

Before passing to an examination of the critical remarks that have appeared recently (1951-1952) with respect to my investigations, I must discuss the essentials of the method used for the determination of electron density. The work of determining electron density can be divided into two parts: 1) determination of the experimental value of the atomic scattering factor for X-rays (f-curve) from a study of the intensity of reflected X-rays; and 2) calculation of the electron density in different directions of the crystal lattice by means of the triple Fourier series, the coefficients of which are values of the atomic scattering factor.

Determination of the f-Curve. The most laborious part of the investigation is the experimental part, which demands a series of carefully performed experiments, the accumulation of a large amount of experimental material, and very careful treatment and critical evaluation. The following two conditions must be observed so that the experimental f-curve can be used for calculation of the electron density. First, it is necessary to make sure that individual values of f are determined with sufficient accuracy. On this accuracy the accuracy of the electron density distribution curve mainly depends. This accuracy is determined by a number of experimental conditions, which are well known. The determination of f-curves, in its relation to experimental procedure and the effect of various factors on the experimental error, has been studied by a number of authors.

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In our investigations we have used the photographic method for the determination of X-ray intensities; we have used this method previously in the study of disorder-order transitions in solid solutions; and it has been used also by a number of authors for the determination of f-curves. In the investigations of Grimm, Brill, Hermann, and Peters [5] an ionization method was used for the measurement of intensities. In the determination of intensities for the construction of f-curves, both methods, photographic and ionization, are practically equivalent in value. No difficulties have been found as yet in the accurate measurement of intensities by either of these methods, and the errors in measurement associated with these methods are sufficiently small to be neglected in view of the fact that errors of another kind are undoubtedly of greater importance in the determination of f-curves.

For the measurement of X-ray intensities, the choice of the form and state of the material under investigation is of importance. We take finely crystalline samples of the material, since extinction, which is difficult to take into account in large crystals, can be completely eliminated in sufficiently fine crystals. Extinction is almost completely absent in aluminum and other substances that have been investigated so long as the size of the crystals is of the order of 10^{-5} cm. Considerable difficulties are met in the preparation of such samples. We have used three methods for these preparations: 1) films of aluminum and copper were prepared by condensation of vapor in high vacuum; 2) nickel powder was prepared by reduction of the oxide with hydrogen; 3) powders of the compounds NiAl and Mg_2Si were prepared by grinding in an agate mortar. In all cases the powders were passed through a sieve having 200 mesh per inch, and washed with toluene. The particles of the powder were measured in a measuring microscope; they were of the order of $3\text{-}6 \times 10^{-4}$ cm. Control X-ray studies of the powders after suitable thermal treatment enabled us in all cases to show that strains were absent and that the grain size was of the required order. The preparation of a suitable sample is the most vital and difficult part of the problem of determining f-curves.

For our X-ray studies we used samples both of flat and of cylindrical form. Use of the flat form permits the absorption factor to be determined relatively simply. Cylindrical samples were used in the determination of weak lines of low and closely arrayed values of θ; and they were not more than 0.2-0.3 mm in diameter, so that it was possible to take absorption into account. The X-ray photographs were taken and developed by the usual methods, care being taken to maintain conditions constant. A blackening curve was obtained for the photographic film used, and this was used in selecting the exposure and development conditions. The conversion from relative to absolute values of the atomic scattering factor was carried out by the method of substitution by a standard substance, usually aluminum, in a special camera.

The calculation of the electron density will be as complete as possible if the number of terms of the series is infinitely great. In practice it is possible to limit oneself to a finite number of terms, for experimental results obtained with a definite degree of accuracy do not permit the low amplitudes of Fourier terms of high order to be taken into account. It is, therefore, necessary to find the sum of a number of terms of the series, such that the last of these terms corresponds to the accuracy of the only experimentally determined quantity—the atomic scattering factor. The value of the atomic scattering factor of aluminum can now be determined accurate within $\pm$ 0.05. The number of terms must be taken so that the coefficients of the last of them are equal to this error. The number of terms obtained in the Fourier series will depend on the number of reflections obtained on the X-ray photograph, and this will depend on the wavelength of the radiation used. For example, for aluminum the use of FeK_α radiation will enable 64 terms to be obtained, the use of CuK_α will give 136 terms, and the use of MoK_α will give 698 terms. The atomic scattering factor for the last terms of the series will be 5.69 for FeK_α, 5.26 for CuK_α, and 0.85 for MoK_α. Hence, even the use of hard molybdenum radiation cannot lead to sufficiently low amplitudes in the last terms of the series. The error introduced into the calculation of electron density by this limitation of the number of the terms in the series has been called the "finite series error". It becomes greater as the radiation used becomes softer, and it can introduce considerable errors in the determination of electron density.

Calculation of Electron Density. The experimentally obtained f-curve can be used to calculate the distribution of electron density in the crystal lattice. The electron density in the crystal is a continuous periodic function of the spatial coordinates, and can be regarded as a function of one or of two coordinates, leading to a one-dimensional or two-dimensional series, i.e., to a projection of the electron-density distribution on a direction or plane in the crystal lattice. Both of these cases are of limited application, since it is not always possible to choose directions in the crystal so that projections of electron density do not overlap and only atoms of one sort are projected at each point. When we treat electron density as a function of three coordinates, we obtain a three-dimensional series characterizing the spatial distribution of electron density. For the calculation of the spatial distribution of electron density a triple Fourier series of the following form is used:

$$\rho_{xyz} = \sum_{h} \sum_{k=-\infty}^{+\infty} \sum_{l} A_{hkl} \cdot \cos 2\pi \left(h\frac{x}{a_1} + k\frac{y}{a_2} + l\frac{z}{a_3} \right) .$$

(h, k, l are numberical indices varying from $+\infty$ to $-\infty$; a is the lattice constant; A_{hkl}, the Fourier series coefficient, is given by $A_{hkl} = \frac{1}{V} \cdot f_{hkl}$, in which V is the volume of the elementary cell; f is the atomic scattering factor, obtained from the experimentally determined f-curve). The zero term is calculated from the condition $f_0 = z$ (z is the total number of electrons in the atom). The only difficulty in the calculation of electron density is the "finite series error", which, as already indicated, cannot be eliminated by experimental methods; it can be eliminated only by calculation methods.

One of these methods consists in lengthening the experimentally found f-curve in the direction of greater values of $\sin\theta/\lambda$ by the extrapolation method proposed by Froman. This method cannot be regarded as sufficiently reliable, since the curve is continued beyond the limits of experimentally determined values of f and cannot be checked experimentally; also, the lengthening of the f-curve leads to a considerable increase in the number of Fourier terms and makes the task of summation much more difficult.

A second method was proposed by Grimm, Brill, Hermann, and Peters [5] under the name of the "calculation temperature" method; it consists in mathematical treatment of the amplitudes of the Fourier series so that the values of the last of them shall not be greater than the error in the experimentally determined atomic scattering factor. The mathematical treatment consists in multiplication of the atomic scattering factors by a temperature factor which adjusts the f-curve to a definite "calculation temperature". The error so introduced into the determination of electron density can be determined only by calculation. Calculations of this sort have been made by Hermann [5] in 1940, Kritskaya and Rovinsky [13] in 1948, and Ageev and Ageeva [8] in 1948.

Finally, we must refer to the mixed method proposed by Kritskaya and Rovinsky in 1948 [13], in which, on the one hand, the f-curve is somewhat lengthened by calculation by Hartree's method, and, on the other hand, this partly experimental and partly theoretical curve is adjusted to the calculation temperature by the method of Grimm and coworkers [5]. This mixed method has all of the errors of the two methods that we have examined, and has no advantages over them.

Significance of the Results Obtained

Among the results derived from experimental studies of electron density, the most interesting and important are not those which merely confirm what was known before this method of investigating the chemical bond was used, but those which yield new, previously unknown facts; these facts include:

1. The presence of "bridges" of electron density (homopolar bond), which unite chlorine atoms in ionic lattices of the sodium chloride type.

2. The presence of "bridges" of electron density in lattices of the diamond type having directed homopolar bonds in the direction of the lines joing the atoms (110 direction).

3. The presence of "bridges" between individual molecules in the molecular-type lattices of organic compounds (hexamethylenetetramine, oxalic acid).

4. Determination of the positions of hydrogen atoms in the lattices of organic compounds (hexamethylenetetramine).

5. The presence of irregular electron distribution and "bridges" in metal lattices (magnesium, copper, nickel).

6. The presence of incomplete ionization in metal lattices (aluminum).

7. The presence of "bridges" of electron density of various intensities (characteristic of the strength of the bond) between various atoms of the complex lattices of metallic compounds (NiAl, Mg_2Si).

8. The presence of asymmetrical deformation of the electron envelopes of atoms in the lattice of the metallic compound Mg_2Si.

These facts are of undoubted interest for the development of the theory of the structure of substances, and they permit a number of general inferences to be drawn.

The crystal structures of even the most simple substances are complex with respect to the nature of the chemical bonds present, and chemical bonds of a saturated type rarely exist in crystals. An examination of the distribution of electron density indicates the complex nature of the chemical bond in simple substances (sodium chloride, magnesium, copper, nickel). In no case is it possible to regard the complex chemical bond in a crystal as the simple sum of elementary types of chemical bonds. A knowledge of the distribution of electron density in crystals permits us to construct a model of the continuous change of the valency state of atoms in crystal lattices.

Reply to Criticisms

The first criticism of the method of determining electron density with the aid of Fourier series was made by Konobeevsky [14] in 1951. The essence of this criticism is as follows:

1. "The practical necessity of prematurely terminating the series, which is a result of the limited nature and slow extinction of the X-ray diffraction spectrum, has led to the idea of introducing an artificial factor that falls as the value of n increases, and this is equivalent to the introduction of an element of indefiniteness into the position of diffraction spectra [7-9, 5]. This will clearly distort the actual distribution to such a great extent [3, 13] that the method becomes of doubtful value."

2. "However, even if the summation could be performed quite correctly, the result could not be regarded as satisfactory in itself, for, in order to draw any conclusion from it that would have physical significance, it would be necessary by some method or other to separate the individual atoms from the distribution obtained. No theoretically based rules are known whereby this process could be effected."

On a number of occasions doubt concerning the electron-density method has been expressed by Boky [15], who has stated: "There are yet no direct and sufficiently accurate methods for the determination of electron density in the outer parts of molecules, although there is a direct and adequately accurate method for the determination of the positions of atoms in molecules."

Finally, in 1951 a paper by Snow [16] appeared in which a critical examination was made of six papers by me and my coworkers on the determination of electron density. The following points are advanced:

1. "In view of the extremely large artificial temperature factors used by Ageev and Ageeva, it is quite possible that the electron densities of the outermost electrons are increased somewhat and, therefore, at a point midway between nearest neighbors, even for truly spherically symmetrical atoms, there will appear an increase in electron density which may seem to be due to bridge bonds, but which will actually be caused by the summation of the overlapping density distributions of the outer electrons of the spherical atoms .... The 'bridges' found may, therefore, be entirely due to the method of calculation used by Ageev."

2. "It seems overly optimistic to place any reliance on an electron-density difference of 0.04 e/A^3 as being meaningful, or to suppose that anything very valid can be said about the valence of metallic aluminum no matter how the data are mathematically treated."

3. "Ageev and co-authors' choice of radiation for the work on copper, nickel and AlNi is particularly unfortunate, since the dispersion corrections are large for the long-wavelength radiations used, and the uncertainties in these corrections are large enough easily to mask the differences in intensity of low-order reflections due to the outer electron distribution."

In 1952 Konobeevsky [17] stated in a paper read at a conference on the theory of alloys:

1. "It has been proposed that an ever-decreasing factor should be introduced into the series, which is equivalent, in many cases, to the introduction of a very significant conventional temperature. This method not only permits one to manage with a comparatively small number of interferences, but also avoids calculation errors associated with the appearance of a "finite-series wave". It is not clear, however, whether the dwindling of the factor is not accompanied by the disappearance of essential variations in the distribution that is being analyzed. It must be pointed out also that fine differences in electron-distribution curves, representing various peculiarities of chemical bonds, are revealed in the form of still finer variations in structural amplitudes. This demands very careful measurement of X-ray interferences and the taking of all factors that may affect the intensity (extinction, absorption, etc.) into consideration."

2. "Difficulties arise also in the interpretation of the resulting projections or cross sections of electron density. Thus, N. V. Ageev treats the increase in density between two neighboring atoms of a metallic crystal as a manifestation of the presence of a special electron "bridge" corresponding to particularly strongly directed bonds. This effect, however, can be treated also as the simple superposition of the electron envelopes of two neighboring atoms."

3. "The method by which the number of free electrons in the crystal is calculated is a very doubtful one .... It is completely arbitrary, and therefore, many results obtained by its aid are, as we shall show below, incorrect."

All these criticisms center around the following points:

1. The effect of the temperature factor on the picture obtained of the electron-density distribution, including the "bridges".

2. The interpretation of the "bridges" of increased electron density.

3. The possibility of determining the degree of ionization of atoms in metal crystals on the basis of the picture of electron-density distribution.

4. The experimental conditions, and the errors that depend on them.

We shall now reply to these criticisms.

1. The effect of the temperature correction on the resulting picture of electron-density distribution was examined by us for the case of aluminum. Our calculations showed that the temperature correction affected mainly the position of the maximum of electron density at the point corresponding to the crystal lattice point. There were no changes at all in the electron density at points sufficiently far removed from the lattice point, i.e., lying in the interionic space. The only exceptions were values of electron density calculated without introduction of a "calculation temperature" or by use of a low value of this temperature, when the finite series error was significant. Already at a "calculation temperature" of 500°, there is no change in the electron-density distribution in the interionic space, in which the valency electrons that are of interest for us are to be found.

Our calculations for aluminum, published in 1948, convinced us of the possibility of using the "calculation temperature" to eliminate finite series errors. In our subsequent investigations on electron-density distribution we made no detailed calculations to justify the calculation-temperature method that we used, as we considered that the results obtained for aluminum showed that it gave rise to no doubts. Since doubt has now been expressed concerning the possibility of using this method without distortion of the results on the electron-density distribution, it is necessary to make a more detailed examination of the effect of the calculation temperature. Let us examine the proofs that have been offered of the impossibility of using the calculation temperature without distorting the calculated electron density.

Konobeevsky considers that the calculation temperature may obscure important distribution differences that are the subject of the analysis. In support of his assertion Konobeevsky refers to the work of Kritskaya and Rovinsky [13], which leads to the conclusion that the "calculation temperature" introduces appreciable distortion into the calculated electron-density distribution. This work, however, contains defects, which are so serious that the authors' conclusion can be disregarded.

In the first place, the authors come to the incorrect conclusion that agreement of experimental values of the atomic scattering factor with the theoretical curve, calculated by Hartree's method, forms a criterion of the correctness of the experimental results. Such agreement, although of interest, cannot confirm the reliability and accuracy of results obtained experimentally. It is, therefore, unsound to lengthen the experimental $\underline{f}$-curve with the aid of values of the atomic factor calculated theoretically by Hartree's method. No basis can be found for this method, nor is it possible to determine the error introduced by this method of manipulating the experimental results. This half-experimental, half-theoretical curve cannot give a true picture of the electron-density distribution. The theoretical Hartree curve for the atomic factor is obtained from a definite, given electron distribution, and it is obvious that the reverse calculation of electron distribution from this curve must give the original, given picture of the distribution. The invalidity of this method of combining experimental and theoretical curves will be obvious from what we have said. The electron-density distribution obtained from a "mixed" curve of this sort must give a picture that is also mixed: it will not be in accord with our theoretical postulates and cannot be regarded as resulting from experimental data: it is rather a distortion of both.

In their interpretation of their results, Kritskaya and Rovinsky [13] make the assumption that in the copper crystal the atoms are in the univalent condition. On the basis of this unfounded supposition, they make calculations that are inconsistent with their hypotheses and conclude that the picture has been distorted by the temperature factor. The authors, moreover, consider that they have in this way made a quantitative estimate of the distortions, on the basis of which they introduce corrections.

Finally, the authors calculate the electron density to the third place of decimals, which is considerably beyond the possible accuracy of the determination of the $\underline{f}$-curve, and on this accuracy the accuracy of the electron-density calculation depends. At present the $\underline{f}$-curve can be determined for aluminum accurate within $\pm$ 0.05; for copper the accuracy is still less. The electron density can be determined with the same accuracy. Calculation of the electron density to the third place of decimals cannot, therefore, be justified.

It will be seen from the above that Kritskaya and Rovinsky's results [13] must be accepted with great caution, and their conclusions even more so, although it follows from their results that at a sufficiently large distance from the center of an ion the electron density is independent, within experimental error, of the "calculation temperature". The doubts raised by Konobeevsky [18, 14, 17] have, therefore, little basis, and they are in conflict with the experi-

mental results and the conclusions that may be drawn from them.

We pass to an examination of the arguments advanced by Snow [16] in support of his opinion regarding the inadmissibility of the use of the "calculation temperature". Snow considers that the bridges of increased electron density found by us can be attributed entirely to the method of calculation that we have used. In his opinion the "calculation temperature" increases the electron density at the point half way between neighboring atoms, and, as a result of the summation of overlapping electron-density distributions of spherical atoms, it causes an apparent bridge bond. In support of his point of view Snow makes some simple calculations. He considers the electron-density distribution for spherical atoms disposed at great distances apart in the lattice. He then moves them to the distance corresponding to the disposition of the atoms that are closest together in the lattice and makes a summation of the electron density at individual points, thus obtaining values that agree with those found by us experimentally, which leads him to the conclusion that the bridges are the result of the method of calculation. This sort of proof cannot withstand criticism. Snow, in using such a method of calculation, is asserting — consciously or unconsciously, I do not know — that 1) atoms have spherical symmetry; 2) atoms remain unchanged with respect to electron-density distribution when they enter a crystal lattice; 3) the electron-density distribution of an atom is independent of its position in the lattice. 4) the electron density in a crystal lattice is the result of a simple summation of the electron densities of the separate atoms.

All four assertions are incorrect. Such atoms are unknown to modern science. Modern science teaches us that an atom is variable, and that its state depends on the surrounding conditions (including its position in the lattice), the spherical symmetry of an atom being only a particular case of its form, which depends on the medium. A crystal cannot be regarded as the simple sum of its atoms. It is impossible to treat a separate atom in a crystal and study it apart from the conditions of its existence, just as it is impossible to compound the separate atoms together on the assumption that the simple sum of them comprises the crystal lattice. In actuality, atoms, in forming a crystal lattice, undergo change. They interact, pass into other states, and change their form. The crystal lattice is formed as a result of the conflict between two tendencies: attraction and repulsion between the electron envelopes of atoms. According to the strength and nature of the interacting atoms, one or other characteristic of the chemical bond may be manifested.

2. Let us pass to the question of the interpretation of the observed "bridges" of increased electron density. In order to obtain a correct explanation of the "bridges" of increased electron density it is necessary to establish correct principles from which to start. As already pointed out, it will be correct to regard the crystal as a single whole, and not as the simple sum of its atoms. An atom in a crystal must be treated as being in a state modified by surrounding conditions. The nature of the interaction of atoms is determined by the result of the conflict between two tendencies: attraction and repulsion of electrons.

From the point of view of these principles, the determination of electron density is a good experimental method. In the application of this method it is not necessary to start from any assumptions regarding the form or state of the atoms, or the nature of their interaction. By measurement of the intensity of X-rays scattered by the crystal — and the scattering is actually produced by the electrons of the atoms — we may determine the curve of electron-density distribution for any directions in the crystal. The resulting electron-density curve may be regarded as a curve showing the probability of finding an electron in one or other place in the crystal lattice. This method, therefore, does indeed treat the crystal and the electrons distributed within it as a single whole; it does not separate individual atoms, but gives only the curve showing the probability of finding the electrons of atoms composing the crystal lattice; it gives a topographical picture of the electron-density distribution, and it reveals the places of increased and reduced electron density.

Only in this way is it possible to interpret the picture obtained of the electron-density distribution: it is obtained by a direct experimental method and is a picture of the actual distribution of electrons (or probability of finding an electron) in the crystal lattice; it exists irrespective of any assumptions and hypotheses concerning the form and state of the atoms, etc. Hence, in accordance with modern ideas concerning the chemical bond, the lines of high electron density between the atoms (bridges) correspond to the highest binding force. Treatment of the places of increased electron density as the result of the simple superposition (summation) of electron densities leads to the necessity of treating the atom as unchangeable and spherical, which is contrary to modern scientific ideas.

3. With respect to the possibility of determining the degree of ionization of an atom from a study of electron density, two objections have been made.

Konobeevsky [17] considers that the method by which we calculated the degree of ionization of aluminum atoms is doubtful and arbitrary. The method that we have used is, of course, to some extent conditional in character, but it has quite a sound basis, and, moreover, methods of this sort are often used in all sorts of calculations in crystal-

lography. Thus calculations and operations made with atomic radii are also conditional in nature, but no one would assert that this method is doubtful or arbitrary. The conditional nature of the method arises from the difficulty in the exact separation of the space occupied by ions from that occupied by conductivity electrons. The boundary between ions and conductivity electrons is, of course, a conventional one, as all of our studies on the determination of electron density have shown, but the error introduced into the calculation by the inaccuracy in the determination of this boundary has, according to our calculations, no effect on the final result. It is, of course, impossible to give an absolute significance to the resulting values. It may, however, be asserted that the ionization of an aluminum atom present in a crystal lattice is incomplete.

Snow [16] considers that it is overoptimistic to treat a difference of 0.04 e/A^3 in electron density as significant and make inferences from it. As we have shown in our work, the determination of the electron density of aluminum is accurate within $\pm$ 0.05 e/A^3, so that it is clear that a value of 0.04 e/A^3 lies beyond the limits of the experimental accuracy. The matter, however, is quite different in our calculation, in which we have used not individual determinations of electron density, but the whole curve derived from nine determinations; not one of these stands outside the limits 0.16-0.24 e/A^3, and they give the mean value of 0.20 e/A^3. There is now no reason to doubt this result.

With regard to the fact that the theoretically calculated atomic factor curves for variously ionized aluminum do not differ, Snow does not take into account that the theoretical curves are constructed on the basis of quite definite assumptions and cannot form a verification of the experimental f-curves. With respect to the effect of valency electrons on the f-curves, it may be pointed out that this effect increases as $\sin\theta/\lambda$ falls, and gradually diminishes as the latter quantity rises. According to our results this effect is appreciable up to $\sin\theta/\lambda = 0.44$, i.e., for the reflections 111, 002, 022, 113, 222, and not only for 111, as Snow asserts.

In concluding this section, I must point out that the result obtained for the degree of ionization of the aluminum atom cannot be regarded as quantitative, but only as qualitative. We may, therefore, insist on the accuracy of our assertion concerning the incomplete ionization of the aluminum atom in the crystal. This is how it is expressed in our paper, and it is only in this way that the results obtained can be interpreted.

4. Snow asserts [16] that we have selected unfavorable radiation requiring a large dispersion correction that may mask small differences in intensity. He criticizes our correction, which was calculated theoretically by Hepple's method, and prefers the experimentally determined correction of Brindley and Ridley, forgetting to point out that the corrections that have been experimentally determined by different authors vary so much that there is no possibility of using them.

Konobeevsky and Mamedov's Method of Trial

In his paper "Investigation of the Structure of Atoms in Crystals by the Method of Trial" Konobeevsky [14] states "... it is not very expedient to attempt to find the actual radial electron-density distribution in an atom (both when free, and particularly when present in a crystal) from the direct measurement of the diffraction spectrum, and subsequently bringing it into relation with the atomic space. A more justifiable method is the method of trial, which consists in the theoretical construction of the function $\rho(P)$, the calculation of the diffraction spectrum F(H), and the comparison of this with experiment. This method of trial can be recommended also because, as we shall see below, it permits us to investigate the function $\rho(R)$ "by parts". The distribution in the atom can be expressed at first in a fairly general form by the introduction of some parameters, in the course of which the symmetry conditions must, of course, be applied. When we pass to the function F(H), this will be found to depend on the same parameters, but for the determination of these it is not necessary to know exactly the whole course of the function F(H); it is sufficient to use only a few points and to compare the separate interferences."

It will be seen from this that Konobeevsky considers the method of trial to be the most perfect method for the solution of the problem of the structure of atoms in crystals. The method of trial, however, has been previously applied fairly frequently for the solution of various problems. Thus, in the determination of crystal structure one assumes the positions of the atoms, calculates the intensities of the X-rays that would be scattered by this structure, and then makes a comparison with the experimental results. But this method of trial is used when there is no direct method. It cannot, in any case, be said to be more perfect. The more perfect methods are the objective, direct methods, such as the recent Fourier series method, which enables us to obtain an objective picture of the distribution and structures of atoms without any preliminary suppositions concerning the nature of this picture. The second advantage that Konobeevsky attributes to the method of trial is also more in the nature of a defect in the method than of one of its merits. In all investigational work, individual measurements are never to be regarded as more trustworthy than the obtaining of a series of functional results. In the second case fortuitous error in the measurement of any quantity can always be readily detected by the nonconformance of the value to the general series of values. When

single measurements are made, this sort of control is absent. The investigation "by parts" of a few points of the individual interferences is a defect in the method of trial.

The results of Konobeevsky and Mamedov's investigation of aluminum [19] are also contrary to the method of trial. According to these results the electrons of an aluminum atom in the crystal tend to move out of the direction (111), and also (110), and into the direction (100), i.e., tend to fill the structurally freest places (octahedral pores) of the face-centered lattice. The "bridges", therefore, are directed not toward the nearest neighbor (110), but along (100). Our knowledge of atomic interaction tells us that interacting atoms approach one another: the stronger the interaction, the shorter the distance, and the greater the electron density between them. According to Konobeevsky and Mamedov's results, the greatest electron density (bridge) occurs in the direction (100), whereas, as is well known, the shortest distance corresponds to the direction (110). Again, the directions (100) and (111) of the aluminum lattice both pass through the octahedral pores, and it is quite incomprehensible how electrons that fill the "structurally freest places" can at the same time move from the direction (111) into the direction (100).

Conclusion

In conclusion it must be pointed out that the method of determining electron density for the solution of the question of the nature of the chemical bond is one of the direct methods for the investigation of this problem. It is deserving of great attention from investigators whose work is directed to the study of the nature of the chemical bond.

The views recently expressed abroad (Snow) and here (Konobeevsky, Boky) with respect to the defects of the electron-density method are erroneous and are in conflict with the experimental data and the inferences that can be drawn from them.

Note. I have not discussed Boky's views because his utterances comprise only a few words expressing doubts concerning the electron-density method, without providing any basis for his opinion.

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* See Consultants Bureau Translation, page 31.

CURRENT EVENTS

ELECTION OF ACADEMICIANS AND CORRESPONDING MEMBERS* AT THE ACADEMY OF SCIENCES OF THE USSR

At a session of the Division of Chemical Sciences of the Academy of Sciences of the USSR held on October 19 and 20, 1953, candidates were selected for election as academicians and corresponding members of the Academy.

At a general meeting of the Academy of Sciences of the USSR held on October 23, 1953, the following were elected by secret ballot as academicians in chemistry: B. A. Arbuzov, V. A. Kargin, V. N. Kondratyev, I. L. Knunyants, and L. N. Nazarov; and the election by the Division of the following corresponding members was confirmed: O. A. Alekin, I. P. Alimarin, K. A. Andrianov, Ya. I. Gerasimov, N. M. Zhavoronkov, M. I. Kabachnik, V. V. Korshak, D. N. Kursanov, P. A. Moshkin, B. P. Nikolsky, A. V. Novoselova, I. V. Petryanov-Sokolov, N. K. Pshenitsyn, A. P. Terentyev, K. V. Chmutov, G. I. Chufarov, M. M. Shemyakin, and N. I. Shuikin.

There were 98 candidates for 23 vacancies as academicians and corresponding members in chemistry. Most of the candidates were registered under special subjects (26 candidates under physical chemistry and 21 candidates under chemical technology). In the preparatory work before the elections it became clear that the academician members of the Division had a difficult task ahead of them: to select the most worthy from a large number of candidates.

New Academicians: Special Subject "Organic Chemistry"

Boris Aleksandrovich Arbuzov is one of our greatest organic chemists, a worthy representative and continuator of the remarkable tradition of the Kazan school of chemists, which is so successfully developing and extending the ideas of A. M. Butlerov. In his 25 years of scientific activity B. A. Arbuzov has worked in a number of fields of organic chemistry, of which three must be given special mention: the chemistry of the terpenes, the chemistry of diene compounds, and the chemistry and structure of organophosphorous and other organometalloid compounds. While making a study of turpentine and derived substances in 1930, B. A. Arbuzov carried out extensive investigations on the chemical reactions of terpenes, which led, after many years of persistent work, to important generalizations and discoveries. His investigations on the isomerization of bicyclic terpenes into terpenes having an open linkage, subsequently known as the B. A. Arbuzov rearrangement, were of outstanding theoretical and practical signficance.

B. A. Arbuzov succeeded in establishing the structure of levopimaric acid, a substance of considerable practical importance, and in so doing he solved a problem upon which some of the greatest chemists of the world had worked for more than 100 years. By brilliant application of the diene synthesis to the proof of the structures of alloocimene and levopimaric acid, B. A. Arbuzov made new and valuable contributions to the understanding of the actual mechanism of the diene synthesis on the basis of modern electronic concepts. With the aid of the diene synthesis he has prepared a large number of new compounds having practical importance in perfumery and in the dye industry (for the preparation of heterocyclic compounds derived from selenophene and thiophene).

The second, and main, direction of B. A. Arbuzov's investigations is the study of the properties, structures, and methods of synthesis of organophosphorus and other organometalloid compounds.

Applying Academician A. E. Arbuzov's classical method for the preparation of phosphonic acids, B. A. Arbuzov synthesized a number of new types of phosphonic acids, containing various heterocyclic rings, thus demonstrating the generality of this method and the possibility of its application to the most varied types of halogen-containing organic compounds.

Valuable results have been obtained by B. A. Arbuzov by application of the parachor method to the study of the structures of esters of phosphoric, phosphorus, phosphonic, dialkylphosphorus, formic, orthocarbonic, and orthosilicic acids, and also of cyclic organic compounds, to which he was the first to apply the parachor method for the determination of fine structure. B. A. Arbuzov obtained material of no less interest and importance by the study

* Photographs of the new Academicians and Corresponding Members which accompany this article in the original Russian journal have not been reproduced in this translation because of limitations imposed by our reproduction process. Publisher.

of organophosphorus and other types of compounds with the aid of dipole moment measurements, which enabled him to draw a number of inferences with respect to their structure and, in particular, with respect to the disposition of allyl groups in space and the possibility of the free rotation of individual groups and parts of the molecules.

Ivan Lyudvigovich Knunyants is one of the highest authorities on the chemistry of heterocyclic compounds; of particular importance are his studies of pyridine derivatives, in the course of which he worked out a number of elegant syntheses (pyridine analogs of Michler's ketone and hydrol, dyes of the triphenylmethane type, etc.). In his work on the synthesis of carbocyanine dyes, which has found practical application, he has made valuable contributions to the chemistry of coloring matters. He has done very important work on an original method for the synthesis of 5-hydroxy-2-pentanone, required in the manufacture of quinacrine and pamaquine. The results of this investigation are already being applied in industry. Knunyants' work on the splitting of epoxides resulted in a number of achievements, including the synthesis of 2-fluoroethanol, which made the syntheses of numerous organic fluorine compounds possible. A similar scission reaction with ethylene sulfide provided material for the synthesis of 2-aminoethanethiols, which are starting substances for the preparation of analogs of certain antibiotics. Somewhat apart from these stand his investigations on the structure of the antimalarial preparations plasmocid, pamaquine, and quinacrine, and the subsequent devising of methods for the preparation of these compounds; particularly important is his so-called "chain" for the synthesis of pamaquine and quinacrine. There can be no doubt that I. L. Knunyants is a very high authority in this field.

In 1946 I. L. Knunyants was elected a corresponding member of the Academy of Sciences of the USSR. In the short time that has elapsed since then he has published more than 25 original papers. Very important investigations described in these include studies relating to the introduction of fluorine into organic compounds, syntheses of hydroxyalkylphosphines, the Beckmann transformation of such complex oximes as those of ionone, the tetralones, and cyclic ketones in general, and studies also of 6-caprolactam, the polymerization of fluoro olefins and unstable cyclic compounds, and the preparation of other macromolecular compounds. His investigations on the addition of hydrogen sulfide and thiols to olefins are very important: the results of these researches have great significance for the synthesis of many physiologically and pharmacologically active substances. Apart from theoretical investigations, I. L. Knunyants has devoted much attention to the study of theoretical organic chemistry, particularly to questions of structural theory.

The third organic chemist to be elected was Ivan Nikolaevich Nazarov, whose scientific activities over the period 1933-1953 have developed in the following directions.

The first group of Nazarov's researches was devoted to the study of free radicals of the aliphatic and aliphatic-aromatic series, namely, the so-called metal ketyls obtained by the action of sodium on branched ketones such as hexamethylacetone and trimethylacetophenone. As a result of these investigations, which revealed the possibility of the existence of stable radicals containing tervalent carbon, a number of studies appeared on the isomerization of olefinic hydrocarbons containing tertiary radicals, which occurs owing to their elimination at comparatively low temperatures.

The second large group of investigations was devoted to the chemistry of acetylene and 1-butene-3-yne. Above all, we must refer to the studies of vinylethynylcarbinols, the simplest member of which is manufactured on the large scale by Nazarov's method and is used for the preparation of new adhesives (Nazarov's "Carbinol Glue"). Vinylethynylcarbinols have served as a basis for the opening of a new field in the chemistry of unsaturated compounds. Among very important applications of 1-buten-3-yne in the preparation of new compounds we may cite the synthesis of vinylisocoumarins and divinyl-ketones, and the cyclization of dienones to give substituted cyclopentenones. The last reaction has been particularly fruitful, since it has made possible the ready preparation of a variety of mono- and poly-cyclic compounds having a five-membered ring.

The third group of Nazarov's researches was devoted to the synthesis of heterocyclic compounds containing a piperidine, pyran, thiopyran, or furan ring from divinyl ketones and allyl vinyl ketones. Some of these were found to be physiologically active, and further work led to the synthesis of a new sedative, promedol, which is more active than morphine and has no toxic properties. Promedol is now prepared on the large scale as a medicinal.

The fourth group of Nazarov's researches was devoted to the synthesis of polycyclic compounds by the use of 1-buten-3-yne; these included compounds related to steroids. He effected the total synthesis of a number of compounds of the cis-cis series having the ring systems of androstane, homoandrostane, estrane, and their heterocyclic analogs. By this means the way has been made clear for the solution of one of the main problems of modern organic chemistry—the chemistry of steroids. Nazarov's work in this direction made it necessary to undertake a number of theoretical investigations relating to the mechanism of the diene synthesis and its sterochemistry. Taken as a whole, Nazarov's work, owing to its purposeful character and its wide scope, is a very great contribution to contemporary

organic chemistry, and it allows us to consider the author to be one of the greatest living organic chemists.

Special Subject "Physical Chemistry"

Valentin Alekseevich Kargin, now elected academician, is a great physical chemist. He is the author of more than 120 papers on various questions in physical and colloid chemistry. In the early years of his scientific activity he made an extensive investigation of colloidal systems, which led to a fundamental change in our concepts relating to the nature and stability of solutions of hydrophobic colloids. In his studies, Kargin showed for the [illegible] time the way in which chemical phenomena play a determining role in the formation and in the stability of s[illegible]ions of hydrophobic colloids – a consequence of chemical change in the surface layer of the colloidal particle during reactions with substances dissolved in the intermicellar liquid. These concepts were subsequently successfully applied by Kargin in the study of ion exchange in soils, in the development of a method for strengthening water-saturated sandy foundations, and in the discovery of a new method for the purification of colloidal solutions and precipitates from electrolytes with the aid of electrodialysis. These two methods are used in large-scale practice.

During recent years Kargin's investigations have been mainly directed to the study of the structure and properties of macromolecular compounds, such as cellulose, plastics, rubbers, and proteins. By his investigations of solutions of high polymers V. A. Kargin has shown that they must be regarded as systems in thermodyanamic equilibrium, and that the dissolution of amorphous polymers should be regarded as a process equivalent to the mixing of liquids.

By means of structural investigations, in which electronographic and X-ray methods are used in conjunction, Kargin has established that cellulose and a number of its derivatives are, in spite of the views of foreign investigators, to be regarded as amorphous. Kargin and his coworkers have carried out extensive investigations on the mechanical and thermodynamic properties of polymers; they have studied relaxation processes occurring in the deformation of polymers, developed methods for estimating the flexibility of polymer molecules, elucidated the mechanism of the deformation of crystalline polymers, and performed a number of other investigations relating to physical chemistry and polymers.

In recent years Kargin has undertaken the task of constructing a theory that will permit us to synthesize polymers of predetermined properties, and he has already obtained a number of important results. Kargin has developed the thermomechanical method of investigation, established the existence of three states in amorphous-liquid polymers (glassy, highly elastic, and plastic flow), discovered the relation between the form of the deformation-temperature curve and the structure of the polymer and its molecular weight, given a quantitative method for estimating the flexibility of polymers from their thermodynamic and mechanical properties, established the peculiarities in the structure of polymer crystals (defects), and studied the mechanism of deformation and shown that deformation is accompanied by a peculiar type of recrystallization. The theory developed by Kargin is used in practice in the synthesis of new polymers having special properties.

Another academician in physical chemistry is Viktor Nikolaevich Kondratyev, an eminent worker on chemical kinetics, the structure of substances, molecular spectroscopy, photochemistry, and other branches of physics and physical chemistry. His principal investigations concern elementary chemical processes and the mechanism of complex chemical changes. Kondratyev is one of the founders of the modern electronic theory of molecules. In this connection particular mention may be made of his investigations on the dissociation of nitrogen, bromine, and salt vapors under the action of electrons and light quanta, and also of his studies of molecular heats of dissociation, and the mechanism of the formation of molecules from free atoms and radicals. In particular, Kondratyev was the first to determine correctly the heat of dissociation of molecular oxygen. It should be noted that already in 1924 Kondratyev applied for the first time the method of mass-spectroscopic analysis in the determination of the dissociation products obtained from salt vapors when bombarded with electrons.

These first researches of the period 1924-1934 already marked Kondratyev as one of those developing the application of modern physics to chemical problems. Kondratyev's further work was characterized to an even greater extent by its leaning toward chemistry. The main line of these investigations was the study of the properties of free radicals and the elucidation of their role in chemical kinetics.

V. N. Kondratyev was the author of a very effective spectroscopic method (line-spectrum absorption method) for the identification and quantitative determination of free radicals. With this method he studied various properties of free hydroxyl and detected the appearance of this radical in many combustion reactions; he also elucidated the important part played by hydroxyl in these reactions. Kondratyev showed that other free radicals, apart from hydroxyl, were formed in many oxidation reactions, for example SO and CS radicals, and he made quantitative studies of their formation and disappearance.

Kondratyev's further investigations led him to infer the presence of large concentrations of atomic hydrogen in the rarefied zone of the hydrogen flame. To confirm this inference he developed a special method for the determination of free atoms during the course of chemical reactions, in which the heating effect occurring at a surface catalyzing the recombination of atoms was utilized. The results obtained by this method fully confirmed the deductions made from the theory. Taken as a whole Kondratyev's researches form the first kinetic investigation in which a systematic study of the separate intermediate substances and their reactions has led to the derivation on a sound basis of the mechanism of a complex reaction and its substantiation by experiment. These studies indicate the direction that must be taken by investigations into the mechanisms of other complex reactions.

New Corresponding Members: Special Subject "Organic Chemistry"

Martin Izrailevich Kabachnik is a specialist on organometallic and organometalloid compounds, on heterocyclic compounds, and on theoretical organic chemistry. Although essentially a worker in synthetic organic chemistry, M. I. Kabachnik has systematically directed his investigations also to the solution of practical questions in the neighboring fields of physiology, biochemistry, medicine, and agricultural science. The greater part of his investigations and inventions are concerned with organic synthesis; he has discovered new chemical reactions and developed new synthetic methods on their basis. For example, he has proposed a method of synthesizing β-halogenated esters of phosphorus acid, 2-haloalkylphosphonic acids and various of their derivatives, and esters of vinylphosphonic acid. These methods are based on the reaction of alkylene oxides with halogen compounds of tervalent phosphorus, which has been studied by Kabachnik. He is to be attributed also with the method of synthesizing 1-haloalkylphosphonic acids on the basis of a new reaction between aldehydes or ketones and halogen compounds of tervalent phosphorus. Recently Kabachnik has developed a method for the synthesis of α-amino phosphonic esters from aldehydes, dialkyl hydrogen phosphites, and ammonia, on the basis of a reaction that he has discovered.

Apart from the development of new synthetic methods, one of the main objects of Kabachnik's investigations has been the discovery of new classes of organic compounds, by the use of which the solution of particular theoretical or practical problems may be possible. He has synthesized the first members of new classes of compounds, such as α-keto phosphonic esters, vinylphosphonic acids, β-halogenated esters of the acids derived from tervalent phosphorus, 2-haloalkyl phosphonic acids and their esters and other derivatives, α-amino phosphonic acids (phosphorus analogs of the biologically important amino acids), dialkyl hydrogen phosphorothioites, derivatives of aminoanabasine, and pyracridones. A number of Kabachnik's investigations are devoted to the solution of theoretical problems of organic chemistry. There are, for example, his studies of the mechanisms of some organic reactions: the amidation of heterocyclic compounds of the pyridine type by means of alkali-metal amides, the isomerization of 2-haloalkyl phosphites by heat, and the reaction of aldehydes with phosphorus trichloride.

The most important of Kabachnik's theoretical investigations are those relating to tautomerism. He was the first to develop a quantitative theory of tautomeric equilibrium and to make an important generalization concerning the reactivities of tautomeric and nontautomeric substances of dual reactivity. On the basis of new theoretical concepts on tautomerism, Kabachnik has carried out a series of experimental investigations, both synthetic and physicochemical, in which he has found confirmation of the concepts that he has developed.

Aleksandr Petrovich Terentyev is the author of well known investigations on the synthesis of heterocyclic compounds of the pyrrole and indole series, which he began in the early days of his scientific activity. A. P. Terentyev is a pioneer in the application of the Grignard method. He has succeeded in applying the sulfonation reaction, previously largely confined to aromatic compounds, to the main types of five-membered heterocycles (furan, pyrrole, indole). He has since developed the method of sulfonating acidophobic compounds, and in this way new classes have become available: sulfonic acids derived from diene hydrocarbons, quinones, furan derivatives, pyrrole, indole, etc. Terentyev and his coworkers have carried out a whole series of investigations on the chemistry of acrylonitrile and dienes, beginning with a study of their polymerization, and finishing with various syntheses.

A. P. Terentyev has carried out important investigations in stereochemistry. Here we must particularly mention the study of the syn-anti isomerism of oximes of heterocyclic ketones. Of special interest are his recent papers on absolute asymmetric synthesis, which have great methodological importance. For a number of years Terentyev has worked on organometallic and complex compounds, and has also discovered and developed a method for the condensation of alcohols inpresence of magnesium. A number of internal-complex compounds of novel structure have been applied by Terentyev as organic analytical reagents for metals.

Mikhail Mikhailovich Shemyakin has a great mastery of theory and experiment in organic chemistry. In recent times he has become the leading Soviet specialist in the chemistry of antibiotics. M. M. Shemyakin's book, "The Chemistry of Antibiotics", already in its second edition, is well known as are the syntheses that he has introduced for synthomycin and levomycetin, the best remedies for typhus, trachoma, and dysentery. Shemyakin has

published a large number of original investigations on various questions of organic chemistry. His theory of the hydrolytic scission of the C—C bond is very important: it has revealed the source, nature, and mechanism of many widely found types of chemical reactions. It may be emphasized that on the basis of this theory Shemyakin has succeeded in elucidating many important transformations of the antibiotics actidone, humulone, streptomycin, and others. In this series the explanation of the formation of maltol from streptomycin is particularly interesting, since it indicates the way in which a straight-chain carbohydrate can be converted into a branched-chain carbohydrate. Shemyakin has succeeded in explaining from the point of view of this theory the essential features of the transamination and α-decarboxylation of amino acids, the β-decarboxylation of amino dicarboxylic acids, and the breakdown of γ-keto α-amino acids and many other reactions of a biochemical nature.

Among other theoretical studies by M. M. Shemyakin, mention may be made of his investigations into the chemistry of aldehydic acids, which completely cleared up the question of the structure of these compounds and made it possible for him to find a general method for the conversion of aldehydic acids into compounds of the quinoline and isoquinoline series. Related to these studies are his investigations on the thermal decomposition of salts, in the first place salts of aldehydic acids, and later of carboxylic acids in general. Shemyakin's investigations on other carbonyl compounds are of importance, particularly those on quinones, which have now led to the development of a general method for passing from a quinone and its derivatives to diketo, hydroxydiketo, and triketo carboxylic acids of the alicyclic and aromatic series.

Shemyakin's investigations on sulfamide preparations (preparation of soluble sulfamides, etc.) are of great practical interest. His studies of the chemistry of vitamins are also very valuable. Shemyakin has made a particularly careful study of the tautomeric transformations in the vitamin B_6 group, and has explained the significance of codecarboxylase in amino acid exchange.

Nikolai Ivanovich Shuikin, a student of N. D. Zelinsky, has worked on the catalytic transformations of hydrocarbons and other organic compounds. Apart from his original theoretical investigations on the dehydrogenational catalysis of hydrocarbons, N. I. Shuikin has carried out a number of important investigations relating to the preparation of individual aromatic hydrocarbons of great economic importance from petroleum. In the same field he has made extensive investigations directed to the detailed study of a complex of questions relating to the problem of the refining of motor fuel by contact-catalysis reactions. Shuikin has developed methods for the preparation of high-quality aviation spirit from the usual straight gasolines and a valuable motor fuel from low-quality sulfurous gasolines.

Shuikin's second important line of work concerns hydrogenational catalysis in the furan series, which has led to a new method for the synthesis of tetrahydrofuransin presence of palladium and nickel catalysts.

Shuikin's third line of work is concerned with the catalytic dehydration of organic compounds, namely alcohols and mixtures of alcohols with amines or ammonia. He has developed methods for the catalytic synthesis of monoalkylanilines.

Special Subject "Organic Chemistry and the Chemistry of Labeled Atoms"

The scientific work of the new corresponding member Dmitry Nikolaevich Kursanov has been concerned with reaction mechanisms and the relation between chemical structure and reactivity in organic compounds. In recent years D. N. Kursanov has extensively and successfully applied the method of labeled atoms in the investigation of these problems.

Kursanov's work on the dehydration of alcohols has thrown light on the course of these important reactions. It has been established that they proceed by a heterolytic mechanism, in which the first, determining step of the reaction is the splitting of a hydroxyl group from the alcohol. In this connection the general nature of dehydrating agents has been elucidated, and the mechanism of possible side processes has been determined.

His second group of investigations include the study of a large number of reactions occurring in presence of aluminum chloride: the Fries rearrangement, the condensation of esters with aromatic compounds (which was discovered by Kursanov), the rearrangement of arylamides, and the new reaction, discovered by Kursanov, of ethyl formate, and also the ethyl esters of some other acids, with benzene, resulting in the formation of 9,10-dimethylanthracene.

A third group of investigations is devoted to a study of quaternary ammonium compounds. Kursanov has discovered a series of new reactions and has determined their mechanisms. According to Kursanov's results, at the basis of the reactions of quaternary ammonium compounds lies their tendency to undergo heterolytic breakdown with formation of a carbonium ion, the electron-accepting properties of which act as the motive power in many alkylation and radical-exchange reactions, etc. These three groups of investigations are unified by the general object of dis-

covering the mechanism of heterolytic organic reactions, the part played by electron-acceptor particles, and methods for their formation or activation. Kursanov has studied the comparative mobilities of hydrogen atoms in 2,4-pentanedione and its aluminum and cobalt derivatives, and also the comparative mobilities of hydrogen atoms in various cyclic and bicyclic ketones. It has been shown that the mobilities of these hydrogen atoms depend greatly on the structures of the ketones and, in particular, on the dispositions of the carbonyl groups and the character of their conjugation with the C—H bonds of neighboring carbons.

Another line of Kursanov's investigations, also carried out with the aid of labeled atoms, is concerned with reaction mechanisms in organic chemistry. In a study of polycondensation reactions it was proved directly that these technically important reactions are accompanied by transesterification at the expense of ester linkages. A study of the mechanism of the cyclization of dienes formed by the hydration of vinylacetylenes in presence of deuterophosphoric acid gave proof of the ionic nature of these reactions, and the determination of the position of the deuterium in the molecule of the resulting cyclic ketone led to important conclusions concerning the structure of the dienes entering the cyclization reaction.

A new and most brilliant discovery by D. N. Kursanov in the field of isotopic hydrogen exchange reactions is that saturated hydrocarbons containing a tertiary carbon atom are able to exchange all of their hydrogen atoms for deuterium in the presence of deuterosulfuric acid, whereas hydrocarbons that contain no tertiary branching are quite unable to undergo hydrogen exchange. On the basis of his experimental results Kursanov has concluded that the hydrogen-exchange reaction in saturated hydrocarbons has a chain mechanism.

Special Subject "General and Inorganic Chemistry"

The work of the new corresponding member, Aleksandra Vasilyevna Novoselova, has been mainly concentrated on the chemistry of rare elements. A. V. Novoselova has carried out extensive investigations on beryllium. She has studied the interaction at high temperatures of silicon tetrafluoride and sodium fluosilicate with beryllium oxide. The application of thermal analysis to the system formed by sodium and beryllium fluorides, and also an X-ray investigation of the phases formed, enabled Novoselova to establish the existence of the previously unknown compound of composition $NaF \cdot 2BeF_2$, of polymorphic modifications in sodium fluorberyllate and beryllium fluoride, and of a new hexagonal crystalline modification of anhydrous beryllium fluoride. Novoselova has made a large number of studies of aqueous systems containing beryllium fluoride and fluorides of other metals, i.e., ternary systems. In practically all of these systems new, previously undescribed compounds were discovered. The results of these studies have helped in the explanation of leaching processes. Apart from the fluoride and its derivatives, she has studied other beryllium salts, in particular, the sulfates. For this purpose two ternary, one quaternary, and one five-component aqueous-salt system formed with sulfates of other metals were studied. Very valuable material was obtained in these experiments, enabling the characterization of a series of new double sulfates. She has also studied systems characterizing the cosolubilities of beryllium chloride with other chlorides in water. The results obtained have considerably extended our information on the complex and double compounds of beryllium. She has carried out a series of investigations on the tensimetric study of beryllium sulfates and nitrates.

For the second vacancy in this special subject, Nikolai Konstantinovich Pshenitsyn was elected. This worker has applied his knowledge to the development of an extremely complex and difficult subject: analysis of the platinum metals. He has carried out an investigation into the rearrangement (isomerization) of complex compounds of platinum, and at the same time he has studied the chemistry of iridium, obtaining a series of compounds that can characterize this element, namely chloronitrites and sulfito salts having extremely characteristic properties. N. K. Pshenitsyn has investigated the hydrolysis of platinum-metal compounds and of compounds formed by platinum metals with oximes. In both of these investigations it is characteristic that the analytical and purely chemical (inorganic) sides are of equal interest, for the hydrolysis process and the behavior of the oximes are found to characterize the individuality of the platinum metals.

Special Subject "Physical Chemistry"

The new corresponding member Yakov Ivanovich Gerasimov is an eminent investigator on the thermodynamics of metallurgical systems. Ya. I. Gerasimov began his scientific work with an investigation of solubility relations in complicated salt systems and heterogeneous equilibria at high temperature. The general aim of the extensive researches of Gerasimov in this field has been the laying of a foundation for the understanding and calculation of pyrometallurgical changes, and the obtaining of their exact thermodynamic characteristics (free energies of formation). He has carried out numerous investigations of the equilibria between hydrogen or carbon monoxide and the sulfides of zinc, lead, copper, nickel, tin, bismuth, and vanadium. He has worked on the problem of liquid and solid solutions at high temperatures and on methods for calculating the activities of the components in binary and ternary solutions in a number of important systems.

In recent years Ya. I. Gerasimov has studied the thermodynamics of the oxides of nonferrous and rare metals, making a comparison of thermodynamic and crystallographic properties. These investigations include work on the equilibria of magnesium, calcium, and manganese tungstates, and of calcium molybdate, with hydrogen. Gerasimov has carried out extensive investigations on the thermodynamics of equilibrium at high temperatures for systems that are extremely important at the present time. He has also made a number of studies in a wide variety of branches of thermodynamics: thus, he has worked on the surface tension of solutions, activities in electrolyte mixtures, and the use of spectroscopic data in thermodynamic calculations.

Igor Vasilyevich Petryanov-Sokolov is well known as a specialist on the physical chemistry of aerodisperse systems. He has invented new precise methods for the quantitative investigation of aerosols, which permit the determination of the size-distribution of the particles and the distribution of electrical charges on the aerosol particles. These methods, which have received general recognition and wide application, have enabled Petryanov-Sokolov and his coworkers to solve some very important questions relating to the electrical properties of aerosols: to elucidate the mechanism of the formation of charges and the laws of their distribution on the particles of the aerosol, to determine the kinetics of the discharge of aerosols in an ionized atmosphere, and to greatly clarify the question of the stability of charged aerosols.

Petryanov-Sokolov devoted an extensive series of investigations to the mechanism of the formation of charges on aerosol particles obtained by the dispersion of liquids. These investigations developed into an independent branch of the science of aerosols, devoted to the electrical properties of aerodisperse systems.

Petryanov-Sokolov obtained extremely important results in his studies of general questions relating to the stability of aerosols and the mechanism of the formation of aerodisperse systems by means of condensation. A whole series of Petryanov-Sokolov's researches was devoted to questions of the precipitation and trapping of aerodisperse systems. Some of the methods that he has developed to counter the action of aerosols have considerable practical significance.

Konstantin Vasilyevich Chmutov is a worker on surface phenomena whose extensive investigations cover gas and vapor sorption at solid adsorbents, the adsorption of dissolved substances, the kinetics and dynamics of sorption, diffusion phenomena, and questions of adsorptional and ion-exchange chromatography. Chmutov's investigations are original in their conception and their execution. He is widely known as a master of delicate physicochemical experimentation.

In an early series of investigations, carried out by Chmutov in conjunction with his teacher, Prof. N. A. Shilov, an original concept was developed concerning the adsorption of electrolytes, regarded as an ion-exchange process with the products of the activated adsorption, or chemisorption, of oxygen (surface carbon oxides). Later, Chmutov showed in some careful investigations that in a number of cases inversion of absorptional sequencies may occur in the adsorption of organic acids or alcohols on finely porous active charcoals as a result of purely spatial obstacles, increasing in magnitude with increase in the length of the carbon chain. The false equilibria that arise in such systems, and may last for decades, can be broken down by disturbing agents, such as ultrasonic fields. The concepts developed by Chmutov relating to the dynamics of catalytic processes in the nonpoisoned and poisoned layers of catalysts were the first theoretical descriptions of these complicated cases of absorption that were based on exact experiment. Great scientific interest is presented by Chmutov's investigations of capillary-condensation processes in artificial capillary systems; they are the most satisfactory of a number of investigations of this sort. The theoretical analysis of the results of numerous experiments on various vapors led to important conclusions concerning the interpretation of experimental results on the capillary condensation of vapors in porous systems. Chmutov devoted much attention to the study of diffusion processes. Among these investigations, his careful study of the temperature dependence of the diffusion of polymers dissolved in monomers is of fundamental importance, and so also is his work on the diffusion and cataphoretic acceleration of the transfer of dyes in gelatin layers, which is associated with the solution of problems of color photography. Among his recent work on kinetics we may mention the quite original investigations on the mechanism of the growth of colloid particles, in which an electron-microscope technique was used in conjunction with a quite new method of "labeled particles", which permitted the mechanism of the coagulation process to be established. The development of the labeled-particle method resulted in an equally original "surface-development" method, which is of general importance for establishing anisotropy in the surface of various colloidal objects.

The scientific interests of Grigory Ivanovich Chufarov are centered around the study of metallurgical processes. All of his theoretical and practical studies relate to the same field: the kinetics and catalysis of chemical reactions and metallurgical processes. Chufarov has carried out and published a series of investigations relating to the hydrolysis of magnesium chloride and the protection of metals from corrosion by salt solutions. His researches were

carried out in close association with industrial organizations, and they rendered vital assistance in the creation of the Soviet potash-magnesia industry. For a number of years Chufarov was occupied with a study of the process of etching of metals and the theory of the action of retardants for this process. His theoretical researches on the etching of metals and on the retarding action of additives were closely associated with the practical requirements of a number of branches of industry. Special mention must be made of the detailed investigation of the phenomenon, which he was the first to observe, of the retardation of the dissolution of iron-silicon alloys in sulfuric acid containing halide ions, which results from the formation of a surface protective film of lower silicon oxides on the metal. Chufarov has also carried out investigations concerned with the etching of metals and the wetting of their surfaces for application in such operations as the galvanizing and tin-plating of iron and the cold drawing of tubing. A very important line of his work is concerned with the kinetics of the reduction and dissociation of metal oxides. In these investigations Chufarov is developing the original studies of Academician A. A. Baikov in a creative manner. Chufarov and his school have developed an absorptional-catalysis theory of the reduction of metal oxides. His work on the reduction of metal oxides is widely applied in scientific institutes and manufacturing organizations.

Special Subject "Hydrochemistry"

The numerous and important investigations of the new corresponding member Oleg Aleksandrovich Alekin have been entirely devoted to hydrochemistry. The first investigations of Alekin were concerned with a comprehensive hydrochemical study of the Terlets mountain lake, and other lakes of this district of the Altai mountain system and their feeders; he later studied the lakes of the Katum ridge. These studies formed the beginning of his systematic investigation of the lakes, and later the rivers, of the USSR. As a result of these extensive investigations, the three-volume monograph "The Hydrochemistry of the Rivers of the USSR" was published. His direct study of the hydrochemistry of rivers and his thorough acquaintance with all previous material on this subject enabled Alekin to solve a number of methodological and theoretical problems in hydrochemistry. Among his experimental hydrochemical investigations are many concerned with the determination of dissolved oxygen, hardness, oxidizability, pH, and gold, etc., in water; he has set up a number of hydrochemical field laboratories and stations. On the basis of his practical experience he has written "Guide to the Chemical Analysis of Inland Waters" and other hydrochemical handbooks of high merit.

Special Subject "Chemical Technology"

Kuzma Andrianovich Andrianov has worked on the synthesis and technology of macromolecular compounds and dielectrics. In 1937 he began to publish investigations on organosilicon compounds, and these resulted in a wide development of the chemistry of these substances. In 1938 his first papers on the mechanism of the hydrolysis and condensation of alkyltriethoxysilanes appeared: in these he first demonstrated the formation of siloxane bonds in the course of the hydrolysis, leading to the formation of macromolecular organosilicon compounds, the polyorganosiloxanes. Andrianov showed that the size of the saturated organic radical had no effect on the chemistry of the condensation process, but was of importance for the rate and degree of hydrolysis of the ethoxyl groups. When an unsaturated radical was present, however, not only the condensation reaction, but also polymerization occurred, owing to the presence of the double bond. These investigations were continued in studies of the polymeric products derived from trichlorophenylsilane and dichlorodiphenylsilane. These various investigations form the basis of the resins, lacquers, and insulation materials developed by Andrianov. In the treatise "Macromolecular Organosilicon Compounds", which appeared in 1949, Andrianov examines methods of synthesizing monomers, questions relating to the reactions yielding polyorganosiloxanes of different types, and the physicochemical, mechanical, and dielectric properties of various polysiloxanes. In 1951 he published papers on the chemistry of polysiloxanes, in which he proposed a condensational-polymerization mechanism for their formation. Andrianov has carried out much work on the chlorination of biphenyl. The most important result of this work was the isolation of a special type of polychlorobiphenyls, a mixture of which had little tendency to crystallize. These investigations formed the basis for the development of a new liquid dielectric, Sovol. In 1932-1935 Andrianov published a series of investigations on macromolecular compounds in which he studied the kinetics of the condensation of phenols with acrolein and other aldehydes in presence of acid and alkaline catalysts.

In his work on the preparation of soluble resins, Andrianov synthesized hexylphenol-formaldehyde (oil-soluble) and aniline-formaldehyde resins. Of exceptional importance is his work on the formation of polyvinylacetal resins and its use as cable insulation ("Vinflex"). His investigations on electrical insulation are well known, they are given both in papers and in separate monographs. In a series of papers he examines general theoretical questions relating to insulation: stability to heat, chemical reagents, and moisture; inflammability, dielectric properties; etc. In these he makes definite inferences concerning the future course of work with the object of obtaining

the most perfect insulators. The new insulating materials developed by, or under the supervision of, K. A. Andrianov are now applied on a large scale in the electrical industry.

Nikolai Mikhailovich Zhavoronkov is a specialist in chemical technology. His main researches have been devoted to the investigation of processes for the preparation of hydrogen and the purification of gases in the production of synthetic ammonia, and to processes for the separation of liquid mixtures by adsorption, rectification, molecular distillation, and chemical exchange. His investigation on the purification of converter gas from carbon monoxide by means of ammoniacal cuprous salts has found practical application in existing works and in new projects.

Zhavoronkov's work on the solubility and absorption of carbon dioxide by water is also applied in industry, and it is of theoretical importance. A series of Zhavoronkov's investigations is devoted to the study, by means of aerohydrodynamics, of the scrubber process, which is one of the very important questions relating to the construction of absorption, rectification, and other chemical apparatus for effecting separations. In spite of the long and extensive application of scrubbers in industry, the scrubbing process, and in particular the aerohydrodynamic conditions under which scrubbers work, have received little study until recently. This gap in our knowledge has been to a great extent filled by the work of Zhavoronkov, who was the first investigator in the USSR to make a general systematic study of the aerohydrodynamics of the scrubber process. His researches have established the general laws relating to the movement of gas in dry and sprinkled scrubber fillings and to the hydraulic resistance of scrubber fillings and finely ground granular materials, thus enabling the productivity reserves of these and catalyst vessels to be determined and an indication of methods of increasing productivity to be found. Zhavoronkov has carried out an extensive investigation in order to establish the physicochemical regularities to be observed in the separation of mixtures by means of molecular distillation. He has developed methods and apparatus for the separation of mixtures by the method of high-vacuum rectification. He has devised an original, highly efficient horizontal apparatus for absorption, rectification and chemical-exchange processes.

Panteleimon Afanasyevich Moshkin is an expert in industrial organic chemistry. His first technological project, the manufacture of iodine from seaweed, was based on his own experiments on the Murmansk coast.

P. A. Moshkin has devised an interesting synthesis of pyridine compounds by the condensation of aliphatic aldehydes with ammonia; this synthesis is still of importance and is used for preparative purposes. His investigations on the oxidation of paraffins to carboxylic acids are of great importance. In the course of these researches other important work was done, such as the preparation of chemically pure palmitic acid, and the study of the operating conditions required for catalysts used in the fat industry. Moshkin's investigations on the separation of phenols from the resin obtained in the semicoking of coal are of great importance. He worked out technical methods for the preparation of polyhydroxybenzenes, catechol, resorcinol, and xylenols. Moshkin developed a method for the preparation of butanediol and a large number of other substances (about 50) from furfural. We must make particular mention of the decarbonylation of furfural, and his process for the continuous hydrogenation of the resulting furan to tetrahydrofuran; under the conditions found the hydrogenation catalyst is active for a very long time. Exceptional interest is presented by his work on the preparation of butyl alcohol from synthetic rubber wastes and on the synthesis of excellent plasticizers or of starting materials for the preparation of plasticizers.

Special Subject "Chemistry of Macromolecular Compounds"

The new corresponding member Vasily Vladimirovich Korshak works on the chemistry of macromolecular compounds. V. V. Korshak combines in excellent fashion the solution of problems of great theoretical importance with the practical application of the results obtained. Most of his researches are concerned with macromolecular compounds, and are mainly devoted to the study of polycondensation processes leading to the formation of various polymers. Korshak and his coworkers have, for example, studied the polycondensation of dicarboxylic acids with diamines, glycols, and amino alcohols, and also of dichloroalkanes with aromatic hydrocarbons: he has found a new type of polycondensation reaction, namely, the transarylation of diarylalkanes in presence of catalysts. On the basis of the results of a large number of experimental investigations, Korshak has constructed a theory of linear polycondensation, which is in good agreement with the experimental results, explains the regularities observed in polycondensation processes, and enables the course of these processes to be controlled. As a result of his study of the polycondensation of dicarboxylic acids with diamines, polyamide resins were obtained, and these are soluble in organic solvents and are very promising for application as adhesives, lacquers, etc. Study of the polycondensation of dicarboxylic acids and their esters with glycols has led to the preparation of polyester resins having good mechanical and dielectric properties. Korshak has established the basic laws of the reactions leading to the formation of polyesters, and these laws are in close accord with the theory of linear polycondensation developed on the basis of his studies of the polycondensation of dicarboxylic acids with diamines. The results of some of Korshak's studies of polymerization have enabled certain generalizations to be made concerning the effect

of the sizes and number of substituents on the tendency of unsaturated compounds to polymerize.

Special Subject "Radiochemistry"

The new corresponding member Boris Petrovich Nikolsky has made original scientific investigations in a number of branches of physical chemistry. His main line of work has been associated with the experimental and theoretical study of ion exchange in heterogeneous systems. Nikolsky was the first to make extensive application of physicochemical methods of analysis in agricultural chemistry, and he initiated fundamental investigations, which are being successfully developed by the school of investigators that he has created. Of great importance is the development by Nikolsky of complex methods for the study of electrolytes in soil extracts: the extensive and accurate results obtained form the basis of his theory of ion exchange in soils. By a generalization from the results of studies on ion exchange a general classification of ion-exchange phenomena into three main types was evolved, and in these the cases of exchange by adsorptional and by chemical mechanisms appeared as limiting cases. For these types of exchange statistical and thermodynamical theories were evolved. Nikolsky gave a general equation covering all cases of ion exchange. These investigations are of importance also from the point of view of the double-layer concept, which was extended to nonmetallic systems (ion-exchange systems). Great scientific interest is presented by the theory that Nikolsky developed for the glass electrode, which is based on thorough experimental investigations and the theory of ion exchange advanced previously. In the majority of these investigations Nikolsky made extensive application of radiochemical methods, a field in which he is recognized specialist. Among other studies, his investigations on the physical chemistry of natural waters are of considerable importance: use of more accurate (in some cases, new) methods of investigation enabled a correlation to be established between the salt composition of natural waters and their physicochemical properties, particularly the pH.

Special Subject "Analytical Chemistry"

The investigational work of the new corresponding member Ivan Pavlovich Alimarin has taken three main directions: the development and improvement of methods for the analysis of minerals and ores; investigations on the analytical chemistry of widely diffused and rare elements, and the development and improvement of methods of micro and ultramicro analysis. His earliest work was related with the search for new methods, having greater speed and accuracy, for the analysis of mineral products; for example, the colorimetric determination of silicic acid in presence of iron, phosphorus, fluorine, etc. He carried out a number of investigations on the analytical chemistry of boron and the rapid and accurate determination of it in silicate minerals and other mineral products. A number of his investigations was devoted to the qualitative and quantitative determination of fluorine in minerals and fluxes. He perfected a method for the determination of constitutional water in micas and other minerals, it was based on the reaction between silicates and sodium tungstate at high temperature. Alimarin set up some mobile field laboratories enabling geologists to carry out qualitative and approximate quantitative analyses of useful minerals under field conditions. Alimarin has paid special attention to questions relating to the determination of elements present in trace amounts. In the solution of this important and difficult problem of analytical chemistry he has made extensive use of various physical and physicochemical methods of investigation, such as spectrum and X-ray-spectrum analysis, photocolorimetry, polarography, amperometry, electron microscopy, and labeled atoms. Alimarin has proposed a scheme for the analysis of micro quantities of minerals, slag occlusions, and the products of mineral synthesis in which a specially developed apparatus and analytical procedure is applied to samples of material weighing 1-20 mg. In recent years Alimarin has successfully developed methods of ultramicrochemistry.

At a session of the Division of Chemical Sciences held on October 19, 1953, papers were read by Academician I. L. Knunyants on "Investigations on Mercapto Amino Acids" and Corr. Memb. Acad. Sci. USSR A. P. Terentyev on "Investigations on Functional Organic Analysis".

At a meeting of the Division held on October 24, 1953, in connection with the termination of his period of office, Academician Mikhail Mikhailovich Dubinin was again elected as Academician-Secretary of the Division.

At a general meeting of the Academy of Sciences of the USSR held on October 26, 1953, Academician M. M. Dubinin was elected as member of the Presidium of the Academy of Sciences of the USSR and his election as Academician-Secretary of the Division of Chemical Sciences of the Academy was confirmed.

A. E. CHICHIBABIN'S "FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY", VOLUME I

I. L. Knunyants

Soviet chemical literature includes a number of textbooks on organic chemistry that have played important parts in the training of specialists in this branch of chemistry. Among such textbooks a leading place is occupied by A. E. Chichibabin's widely known "Fundamental Principles of Organic Chemistry", the last edition of which appeared in 1932 and was translated into foreign langnages. In this book intelligent choice of factual material is combined with a deep and vigorous exposition.

Both from the methodological and scientific points of view, A. E. Chichibabin's book is generally acknowledged to be one of the best in world chemical literature. It gives an exceptionally competent exposition of the mutual relationships between the various classes of organic compounds. It teaches dialectics in action and develops the chemist's mode of thought in the student. All this helps in the rapid acquiring of the colossal factual material of organic chemistry and builds it up into a systematic, easily remembered system.

In the twenty years that have passed, however, Chichibabin's book has in many respects become out of date. In recent years organic chemistry has made considerable progress, and many of the concepts developed earlier have been changed. These are concerned mainly with new reactions and transformations of hydrocarbons and aliphatic derivatives, on the basis of which new branches of chemical industry have arisen. It is natural that the exceptional qualities of this textbook should make it necessary to bring out a new edition, in which it would be necessary to revise and supplement it, mainly with respect to factual material and its theoretical treatment. This work has now been done by the State Chemical Literature Press, with the participation of a large group of Soviet scientists, and Volume I of the book (Acyclic Compounds) has now appeared under the editorship of Prof. P. G. Sergeev.

In the new edition the order of exposition and a great part of the factual material are retained. The principal sections are supplemented by new material that reflects the attainments of organic chemistry in the last two decades. There is, for example, a treatment of recent developments in the chemistry of paraffin hydrocarbons, of new methods of using acetylenic hydrocarbons, and of progress in the chemistry of macromolecular compounds, including natural polymers. Modern views on the mechanisms of the more important reactions are given, and an adequate account is given of the possibilities of physicochemical methods and other modern methods of organic chemistry, and of results of their application. Some important sections have been practically rewritten, for example, the chemistry of carbohydrates. Many sections have been radically revised, e. g., the chemistry of amino acids and proteins, the polymerization of unsaturated compounds, X-ray analysis, and the Walden inversion.

In connection with the development and successful application of electronic concepts in organic chemistry, a new theoretical introduction is given containing an objective historical review of the origins and development of theoretical concepts in organic chemistry. A particularly detailed exposition is given of the origin and development of A. M. Butlerov's theory of chemical structure. Much attention is devoted to modern views on chemical structure and the mutual effects of atoms in molecules. The scientific invalidity of the concepts of resonance and mesomerism are demonstrated. The additional matter in the theoretical introduction is written in full accord with the decisions of the conference on questions of the theory of chemical structure in organic chemistry held by the Division of Chemical Sciences in 1951 and with the decisions of the conference of organic chemists held by the Division of Chemical Sciences in 1953. In general, with the exception of some minor errors, this section is written well and carries the reader up to the present level of theory. Apart from the material expounded in the theoretical introduction, there are theoretical treatments in the main text relating to the subjects treated there.

Organic chemistry is a science on which many branches of industry are based, and the introduction into the textbook of information concerning the technological significance of particular reactions and the main methods of processing and utilizing organic substances must be regarded as correct. The book, of course, does not give an exposition of the technology of any particular manufacturing process, but the possibility in principle of technical syntheses is given adequate treatment (the chemical treatment of petroleum hydrocarbons, the preparation of synthetic rubber and other high polymers from unsaturated compounds, the manufacture of polyamide resins and of artificial and synthetic fibers, etc).

The book is not free from defects and omissions. Among the main defects of the book as a textbook is its considerable size. The increase in size results mainly from the added material in the introduction, the inclusion of tables of the properties of the homologs in individual classes and of short biographies of chemists, and the extension of chapters on carbohydrates and proteins. These increases in size are partially compensated for by the considerable shortening of the sections on the qualitative and quantitative analysis of organic compounds; also, the section on complex compounds has been removed. It must be pointed out also that individual reactions have not generally been given detailed interpretation in terms of electronic concepts, although this should have been done in many cases. The weakest section is that on proteins; here not only is the student presented with some doubtful facts, but there are a few errors in nomenclature (haloalkyl, instead of alkyl halide, etc.). A particularly unsatisfactory feature for a textbook is formed by a number of misstatements and factual errors, which, unfortunately, are rather numerous.

For example, on p. 422, it is stated that in the hydration of ethylene oxide polyethyleneglycols are formed as intermediate products. This misstatement – "intermediate product" instead of "by-product" – can lead to an incorrect understanding of the process. On the previous page the same question is treated incorrectly. On p. 76, an unsatisfactory example is given in illustration of pure geometric isomerism in absence of an asymmetric carbon atom. On pp. 188 and 414, contradictory information is given concerning the application of tetrachloroethane. On. p. 335 an unsatisfactory treatment is given of the use of olefins. On p. 337, haloalkyl is written instead of alkyl halide. In the supplementary notes on p. 424, reference is made to rubberized fabrics impregnated in drying oils, which are not manufactured. On p. 241, an incorrect formula is given for Rongalite, the sulfur being united to the hydroxymethyl group through an oxygen atom. On p. 337, "correctness" is written instead of "laws". On p. 300, NN-dichloroamines are referred to as derivatives of nitrogen trichloride. On p. 301, the bonds are incorrectly represented in alkylarsonic, alkylphosphonic etc. acids. Some of the concepts introduced into the textbook, e. g., the coordinate link, are not provided with a satisfactory theoretical basis. In general, however, the work of the team of chemists on the revision and extension of Chichibabin's book is very praiseworthy. It is to be regretted that in the course of the last twenty years, not a single textbook has been issued that corresponds, in its methodological significance and theoretical level, with the contemporary state of organic chemistry. The present edition of Chichibabin in the main fills this gap. The appearance of Volume I of the revised "Fundamental Principles of Organic Chemistry" is an important event for specialists in organic chemistry, and also for chemistry students, who have at last been provided with a good modern textbook.

LOW-TEMPERATURE MODIFICATIONS OF AMMONIUM NITRATE, AND ITS COOLING AND QUENCHING

S. I. Volfkovich, S. M. Rubinchik, and V. M. Kozhin

In addition to the four crystalline modifications of ammonium nitrate that exist at normal pressure and at temperatures above 0° (I, cubic, 169-125°; II, tetragonal, 125-84.5°; III, β-rhombic, 84.5-32.4°; IV, α-rhombic, 32.4° to − 16°), there are known also one modification that exists below 0° (V, tetragonal, stable below − 16°) and one modification that exists at pressures higher than 9000 kg/sq. cm and temperatures above 169.2°.

There are indications in the literature that a transformation of ammonium nitrate occurs also in the region − 50° to − 65°. Hendricks and coworkers [1], who detected a small anomalous change in the specific volume at − 50°, point out that the X-ray diagrams for ammonium nitrate powder at − 33° and − 78° are very similar. Crenshaw and Ritter [2], who studied the variation of the specific heat of NH_4NO_3 with temperature, obtained a maximum on the specific heat − temperature curve at − 60.4°. In an analysis of these results, Meerman [3] pointed out quite rightly that the curve should have had a maximum at − 16°, since there can be no doubt in the existence of a transition at − 16° (IV ⇌ V); but the authors concerned detected no maximum at − 16°. Meerman considers that there is no transition at − 60.4°, but only retardation of the establishment of equilibrium, which is observed for a number of ammonium salts at low temperatures. Jaffray [4], using the differential-thermal method, found the transition temperature of NH_4NO_3 to be − 57° to − 60°. He noted also a transition in the region − 150° to − 160°, but mentioned this only in passing. Volkringer and coworkers [5] have noted an anomaly in the Raman spectra of ammonium nitrate between − 75° and − 192°.

In view of the meager study that has been devoted to the behavior of ammonium nitrate at low temperatures, we have investigated the transformations of this salt with the aid of differential thermal analysis, microcinematography, and X-ray analysis. Microcinematography of the polymorphic changes of ammonium nitrate was first carried out in the range 170-20° in 1940 by one of the authors of the present paper, working with Glazova [6] in the Laboratory of Scientific and Applied Photography and Cinematography of the Academy of Sciences of the USSR.

EXPERIMENTAL

In the present investigation we have studied the behavior of the salt when cooled to − 196°. We have made use of Tsurinov and Volnova's universal cooling and heating stage in this work, the cooling agent employed being liquid nitrogen. The temperature was determined by means of a fine thermocouple (platinum and platinum-rhodium; d = 0.1 mm).

A 0.001-0.002 g sample of dry ammonium nitrate was placed on a slide, covered with a cover glass, and carefully heated to melting. The fused ammonium nitrate was slowly cooled (1-1.5° per minute) under the microscope in polarized light (magnification 8 x 10), and the four transitions to crystalline modifications were clearly perceived (Figures 1-4).

$$\text{Melt} \xrightarrow[169°]{} \text{I} \xrightarrow[125°]{} \text{II} \xrightarrow[84.5°]{} \text{III} \xrightarrow[32°]{} \text{IV}$$

When the rate of cooling exceeded 2° per minute, only three transitions were observed:

$$\text{Melt} \xrightarrow[169°]{} \text{I} \xrightarrow[125°]{} \text{II} \xrightarrow[50°]{} \text{IV}$$

i.e., when cooling is at more than 2° per minute the modification III is not detected, and instead of the points

84.5° and 32°, the point 50° is found. This transition was recorded on cinecolor film, a very clear picture being obtained

The large polyhedra of II were converted into a needlelike polycrystal (Fig. 5). No visible changes occurred in the polycrystal when it was preserved in a desiccator for 14 days.

In order to clarify the meaning of the pictures obtained by microcinematography, we took cooling curves. On these curves (Figures 6-9), which were plotted for various cooling rates (1.5-30° per minute) and for samples of 0.02-0.15 g, the same breaks were always obtained; they corresponded to the transitions:

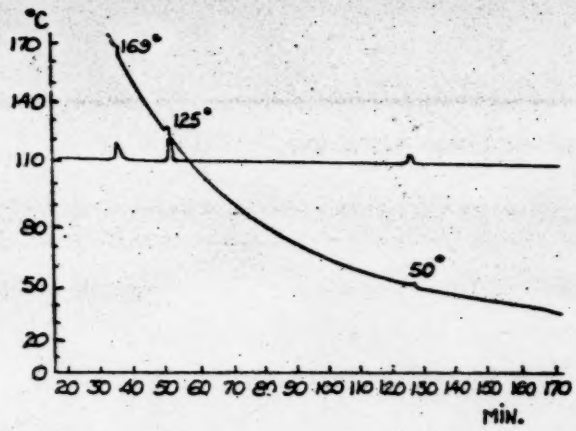

Fig. 6. Cooling curve for NH_4NO_3: R_D* 900 ohms; R_d 740 ohms; cooling rate 1.5°/min; wt. 0.02 g.

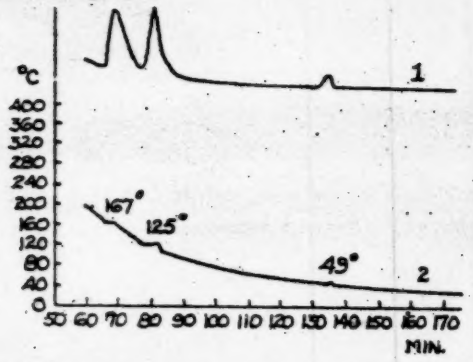

Fig 7. Cooling curve for NH_4NO_3: R_D* 2000 ohms; R_d 150 ohms; cooling rate 1.9°/min; wt. 0.15 g. 1) Differential plot; 2) direct plot.

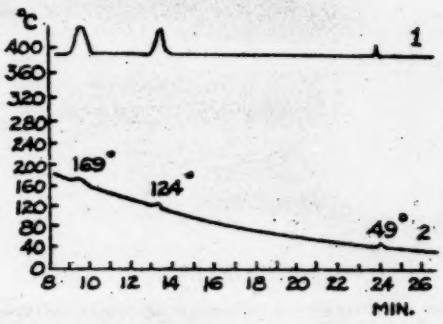

Fig. 8. Cooling curve for NH_4NO_3: R_D* 2000 ohms; R_d 150 ohms; cooling rate 8.3°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

$$\text{Melt} \xrightarrow[169°]{} \text{I} \xrightarrow[125°]{} \text{II} \xrightarrow[50°]{} \text{IV}$$

We were unable to plot the cooling curve for a very small sample of fused ammonium nitrate (0.001-0.002 g, as we took for the microscopic investigation), in which all four transitions should have been found. We carried out trials in which the sample was heated at above 125°, but below the melting point, and was then cooled; the transition $\text{II} \xrightarrow[50°]{} \text{IV}$ was again found (Figures 10 and 11). But we obtained a quite clear indication of the transition $\text{III} \xrightarrow[84.5°]{} \text{IV}$ on the cooling curves of ammonium nitrate preheated at below 125° with samples of the order of 0.02-0.15 g (Figures 12 and 13).

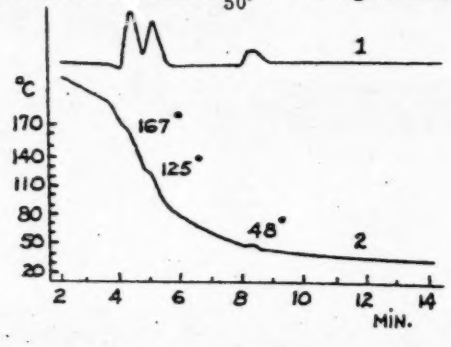

Fig 9. Cooling curve for NH_4NO_3: R* 1000 ohms; R_d 100 ohms; cooling rate 30°/min; wt. 0.05 g. 1) differential plot; 2) direct plot.

The transition at 50° was studied microscopically by Bowen [7], who stated that the transition occurs very readily, both when cooling, and also when heating. According to Hendricks and coworkers [1], the transformation can be repeated many times by heating and cooling, so long as the sample is dry and in the form of a thin film. In a thick layer Modification III is formed after 3-4 transitions. Tiemeyer [8] confirmed this transition by X-ray analysis. He pointed out that it is impossible to repeat the transition $\text{II} \rightleftharpoons \text{IV}$ a large number of times by repeated alteration of the temperature, since

* R_D = Resistance Direct; R_d = Resistance differential.